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# SO-CALLED ANOMALIES AND DEGENERATED ANOMALIES OF ELEMENT (ATOMIC) WEIGHTS*

S. A. SHCHUKAREV

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As we know, D. I. Mendeleyev discovered two anomalies:

1) Tellurium, with an element weight of 127.61, is followed in the system by iodine with an element weight of 126.92;

2) Cobalt, with an element weight of 58.94, is followed by nickel with an element weight of 58.69; in both of these cases the element weight drops instead of rising with successive elements.

Although the element weight served the author of the periodic system as his primary guiding line, at this critical point, when he encountered element-weight anomalies, D.I. Mendeleyev's intuition did not deceive him. He attached prime importance to the principle of the periodical repetition of the form of compounds and chemical analogy, requiring that element weight be subordinated to chemical properties. D.I. Mendeleyev's first move was an endeavor to correct the element weights, as he had succeeded in doing in many cases; but this time, however, not only did his attempt at "correcting the anomalies" remain fruitless, but he discovered a third anomaly: argon, with an element weight of 39.944, preceded potassium, with an element weight of 39.096. And that is the state in which D.I.Mendeleyev left this problem.

We are now justified in asking ourselves how the problem of the "anomalies" appears in the light of modern knowledge. This question is all the more pertinent in that a fourth and a fifth "anamoly" have been established recently. For thorium, whose element weight is 232.12, is followed by protoactinium (el. wt. 231), while uranium (el. wt. 238.07) is followed by neptunium (el. wt. 237).

In particular, it was of interest to set ourselves this problem: which neighbor in the anomalous pair is to blame for the change in the sequence of element weights; is the weight of the first element too high, or that of the following element too low? Or are both partners to blame?

To shed some light on this problem, let us begin by considering two graphs (Figs. 1 and 2), depicting the successive differences between the element weights of the perissads (elements whose atomic numbers are odd) and the artiads (elements whose atomic numbers are even).

We get the following picture.

The law governing the differences between the perissads of low element weight is very simple. In general, the curve tends to stay in the neighborhood of the ordinate 4, i.e., it follows an isodifference course, with the number of neutrons always exceeding that of the protons by one, and with the number of protons and of neutrons both increasing by 2 as we pass

*Presented February 6, 1947 at a meeting of the Chemical Society in commemoration of the fortieth anniversary of the death of D.I.Mendeleyev.

from one element to the next in order.

The slight deviation upward of the chlorine point is due to the presence of the heavier isotope $_{3}$-Cl, which already indicates, moreover, the approach of a long period*; the small interval to potassium, that is, the somewhat smaller difference between the element weights of potassium and chlorine, again depends upon the increased element weight of chlorine. Thus, the rise in the chlorine point is accompanied by a drop in the potassium point. The same conjugation of a pair of displaced points exists in the case of nitrogen and fluorine. If the element weight of nitrogen were close to 15 instead of 14, the difference between $_{15}$ N and $_{11}$B would be represented by a point with the ordinate 4, and the difference $_{19}$F and $_{15}$N would also be 4.

Here we come upon a peculiarity of the start of the system, where four odd elements allow for the existence of stable even-mass subelements whose nucleus contains an odd number of neutrons N and an odd number of protons P, which usually results in radioactivity. As we know, stability of the nucleus requires, in general, that at least one, but better yet, both, of these numbers (N and P) be even.

The four even-mass perissads referred to are:

$_{2}H$ with a $pn$ nucleus; P = 1 and N = 1

$_{6}Li^{3}$ with a $p_3n_3$ nucleus; P = 3 and N = 3

$_{10}B^{5}$ with a $p_5n_5$ nucleus; P = 5 and N = 5

$_{14}N^{7}$ with a $p_7n_7$ nucleus; P = 7 and N = 7

The same cause, i.e., the existence of the even perissad $_{10}B^{5}$, lowers the element weight slightly and, hence, the point denoting boron on the curve of Fig. 1.

The existence of $_{6}Li^{3}$ lowers the lithium point somewhat below 6, where it ought to lie in accordance with the difference between $_{7}Li^{3}$ and $_{1}H^{1}$.

Let us now consider the artiads of the short periods of the system.

Here we have the same picture of the predominance of ordinates with a value of 4, with a slight discrepancy upward for Ne and Mg owing to the presence of heavier isotopes, a slight drop in the case of Si accompanying the rise in magnesium, and only the positions of the beryllium and carbon points attracting our attention by virtue of their singularity. It is evident that the drop in the carbon point is bound up with the rise in the beryllium point, which in turn, depends, as we know, upon the instability of the $_{8}Be^{4}$ isotope, which splits into two atoms of helium, releasing energy.

In contradistinction to the short periods, with their tendency to stay in the neighborhood of ordinates with a value of 4 (isodifference progression), the long periods exhibit the ordinate 6 in addition to the ordinate 4, i.e., the number of excess neutrons begins to rise. In the main, all the points of the perissads lie within the region bounded by 4 and 6, with individual, easily explainable discrepancies, extending to 3 on one hand and to 7 on the other. Only 3 points, corresponding to Pr, At, and Fa, constitute exceptions. The first two of these are extremely low and are explained by the isoneutron regions of the system (especially the isoneutrons No. 82 and No. 126**). The high position of the Fa point is manifest and is bound up with the extremely high growth of the number of neutrons in the transition from At to Fa (10 neutrons to 2 protons), as well as by the low atomic weight of At.

The curve of Fig. 1 may be described as follows in the long-period region: potassium is followed by Sc and V with a normal location of their ordinates (about 6); then there are

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* This assertion is made clearer by the subsequent exposition. It may be noted that chlorine is the first of the perissads with two odd, stable isotopes with uneven mass.

** Cf. the paper "Element Weight as a Periodic Function".

Mn, Co, and Cu with ordinates close to 4, as these elements fall within the isodifference area of the curve $(N - P) = f(P)$. The slight rise of Cu above 4 is due to the presence of the heavy isotope $_{65}Cu^{29}$. The rise from Cu to Ga ought to have been diminished by the heavy isotope of copper, but gallium itself has a heavy isotope $_{71}Ga^{31}$, and therefore the Ga point lies on an ordinate that even exceeds the value of 6.

The As ordinate lies somewhat below 6, as the increased element weight of gallium, due to $_{71}Ga$, affects it. Bromine has the ordinate 5, and, if it did not have the heavy isotope $_{81}Br$, its ordinate would likewise be close to the isodifference value of 4. The ordinate of Rb, lying along the rise in the number of neutrons, would be 6 if not for the influence of $_{81}Br$. Yttrium and niobium lie close to 4, since they satisfy the isodifference. Some depression of the point is due to the heavy $_{87}Rb$. The Tc point is close to 6; rhodium and silver lie on the isodifference plateau* and approximate 4; the rise of the Ag point above 4 is due to the heavy $_{109}Ag$. From silver to indium, as indicated in a previous paper, the rise in the number of neutrons is especially large, and therefore the In point rises above 6 to the ordinate 7. The In point would rise as high as the ordinate 8 were it not for the influence of the heavy $_{109}Ag$. The Sb ordinate is close to 7 and not to 6, since this element not only lies on the rise in number of neutrons, but also possesses the additional heavy isotope $_{123}Sb$. The I ordinate lies below 6 precisely because of the high weight of Sb; Cs and La are close to 6; Pr is markedly lowered for the reason given above; $_{5}Pm$ is close to 6, whereas Eu is lowered to 5 because of the presence of the light $_{151}Eu$; Tb is again increased to 7 owing to the influence of the light $_{151}Eu$; Ho approximates 6. Tm approximates 4 because it falls on the isodifference line; Lu is close to 6, as is Ta, and rhenium is below 6 because it has the light isotope $_{185}Re$; gold lies on the isodifference line, and therefore its point approximates the ordinate 4; Tl is raised to 7, since the transition from Au to Tl corresponds to a large increase in the number of neutrons; were it not for the admixture of the light $_{203}Tl$, the Tl point would go even as high as 8. Bismuth is close to 4, as it lies on the isodifference line; At is below, as it lies on the isoneutron line; Pa is raised very high for the reason set forth above. Actinium and protoactinium lie on the isodifference line, and their points approximate the ordinate 4; neptunium is adjacent to the ordinate 6; Am is on the isodifference line and is at 4.

As we see, nothing in the masses of K, Co, I, Pa, and Np presages the "anomalies" in their element weights.

When we turn to Fig. 2, we see at once that all the causes of the anomalies in the region of long periods are associated with the artiads. The first impression of the artiad curve is that it repeats almost all of the details of the perissad curve; nor could it be otherwise, since we know that the element weights of the artiads and perissads blend into a single monotonously increasing series. The same situation was illustrated by us in a previous paper on the parallel course of the perissad and artiad curves of $N - P$ as a function of $P$.

Like Pr and At, Ce and Po here lie below the ordinate of 3; the Rn point rises to the ordinate 12, as did the Pa point. As with the perissads, the overwhelming number of points lies between the ordinates 6 and 4, with analogous deviations to 7 and 3, depending upon the constitution of the isotope pleiad.

But, at the same time, we see the points Ar, Ti, and Te with ordinates of approximately 8 and even as much as 9 -- let us call them the upper deviations -- and the points Ca, Ni, and Pu below the ordinate 3. Of the last three the Ca point is, at bottom, nothing specific, dropping so low merely as conjugate to the argon point, which has as its principal isotope $_{40}Ar$, with a mass that is higher than that of the expected $_{36}Ar$. If argon consisted solely

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* Cf the paper 'Element weight as a periodic function'.

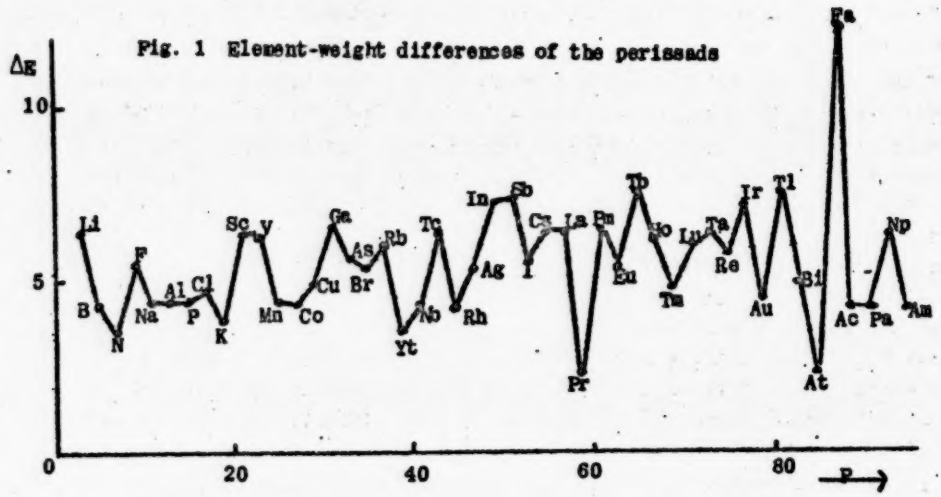



Fig. 1 Element-weight differences of the perissads

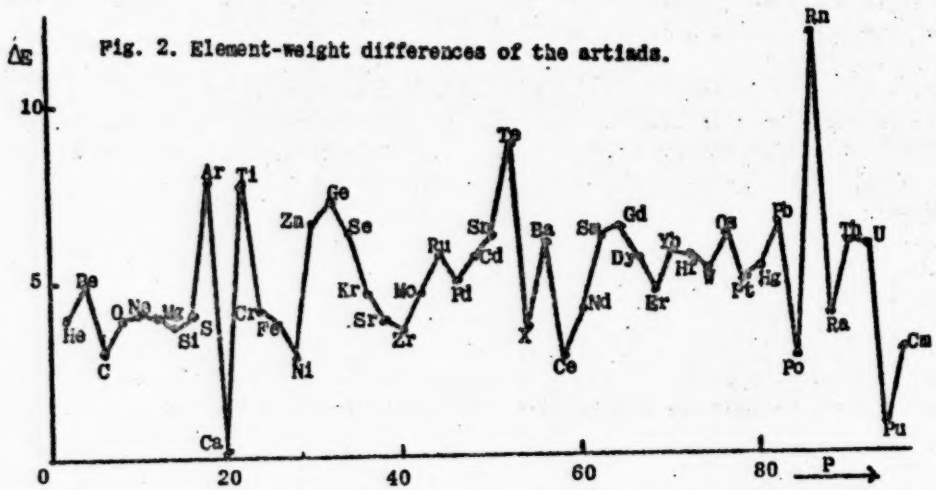



Fig. 2. Element-weight differences of the artiads.

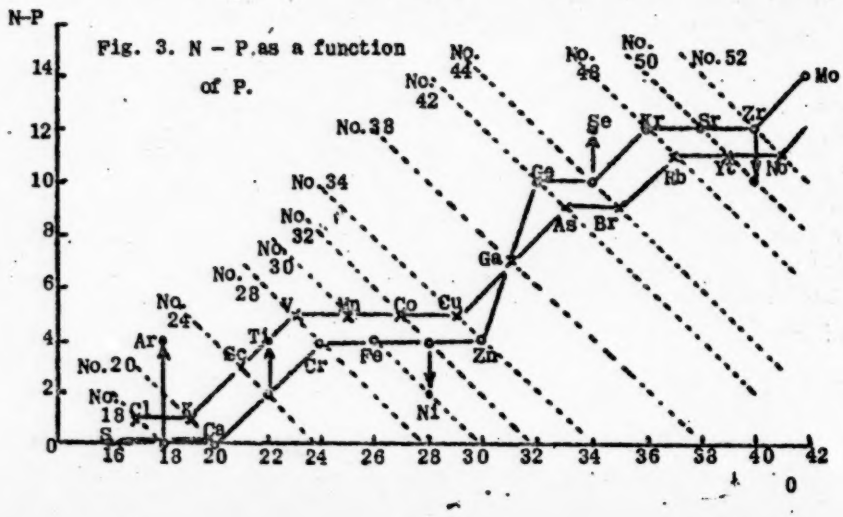



Fig. 3. N – P as a function of P.

of the $_{36}Ar$ atom, the argon point would have the ordinate 4 ($_{38}Ar - _{32}S$) instead of the ordinate 8; Ca would then also have the ordinate 4 ($_{40}Ca - _{36}Ar$). Thus, of the independent lower deviations that are not conjugates of the upper ones, we now see that there are but two: Ni and Pu.

The fact of the presence of such classical examples as Ar, Te, and Ni among the cited upper and lower deviations is strikingly apparent, of course. What is unclear at first sight, however, is why no upper aberrations are to be seen in Th and U, constituting anomalies with Pa and Np; it is not at once understandable why the lower aberration of Pu did not result in lowering its weight below that of Np, as was the case with nickel and cobalt.

It may be shown, however, that the reason for this is the intersection of the artiad and perissad curves at the gallium point. In fact, as is evident from the $(\underline{N} - \underline{P}) = \underline{f}(\underline{P})$ diagram*, up to gallium the artiad line is 1 excess neutron below the perissad line, whereas after gallium the positions of the two lines are interchanged. For the sake of clarity, we reproduce a part of this graph here, representing the region from sulfur to niobium, i.e. covering gallium and the adjacent area, inclusive of Ar, Ti, Ni, Se, and Zr.

On the artiad line the little circles denote the subelements that would be major isotopes if there were no shifts up or down; the dots represent the actual, most widely distributed isotopes.

The formation of anomalies in the sequence of element weights requires that the principal isotope of an artiad element deviate either up from the main channel (an anomaly dependent upon an upward shift, or an upper anomaly) or down (a lower anomaly). In an upper anomaly (such as $Ar^{18} - K^{19}$) the element weight of the next perissad ($K^{19}$) may be smaller than the weight of the preceding artiad ($Ar^{18}$); in a lower anomaly (such as $Co^{27} - Ni^{28}$), on the other hand, the weight of the preceding perissad ($Co^{27}$) may be higher than that of the succeeding artiad ($Ni^{28}$).

It is quite clear that the region from the beginning of the system up to gallium is particularly favorable for the formation of lower anomalies, as the artiad curve lies below the perissad curve in that region. Let us not forget that the normal major isotope of an artiad element and the principal perissad that precedes it both lie on the same isoneutron (as $Co^{27}$ and $Ni^{28}$ on isoneutron No. 32), the mass of the artiad ($_{60}Ni^{28}$) always being one unit higher than the mass of the perissad. Hence, all that is needed to produce an anomaly is a slight shift of an artiad downward; the $_{58}Ni^{28}$ atom is lighter than $_{59}Co^{27}$.

After the intersection at gallium the artiad curve runs above the perissad curve, and hence the formation of lower anomalies is rendered more difficult. In fact, above gallium an artiad lies on the same isoneutron line as the subsequent perissad and not the preceding perissad: $_{92}Zr^{40}$ and $_{93}Nb^{41}$, for example, lie on the isoneutron 52. The preceding perissad now lies on a different isoneutron 50, and has a weight that is three units lower than that of $_{92}Zr^{40}$. That is why the formation of an anomaly requires that the major isotope descend to $_{88}Zr^{40}$, and not to $_{90}Zr^{40}$, as is actually the case. In fact, between Zr and Yt we have merely a degenerate anomaly, so to speak, i.e., not a lowering of the element weight, but merely a markedly smaller increase of the latter. In fact, we might expect an element weight of approximately 92 for zirconium, and a difference of three units between $_{89}Yt$ and $_{92}Zr$. In truth, the light isotope $_{90}Zr$ predominates, despite the presence of the heavy isotopes $_{92}Zr$ and $_{94}Zr$ in the isotope pleiad of zirconium, and the element weight of Zr is 91.220, i.e., it is only 2.30 units higher than that of Yt.

For the same reason, all the other lower deviations that exist above the gallium intersection produce no anomalies in the series of element weights, since these anomalies are degenerate, as it were.

We list the degenerate lower anomalies as follows:

---

* Cf. Paper cited.

1) Yt 88.92 $\Delta$ = 2.30
Zr 91.92 (instead of 3)

2) Pr 140.92 $\Delta$ = 3.35
Nd 144.27 (instead of 5)

3) Ho 164.94 $\Delta$ = 2.26
Er 167.2 (instead of 3)

4) Ta 180.86 $\Delta$ = 3.07
W 183.93 (instead of 5)

5) Ir 193.1 $\Delta$ = 2.13
Pt 195.23 (instead of 3)

6) Au 197.2 $\Delta$ = 3.41
Hg 200.61 (instead of 7)

7) Np 237 $\Delta$ = 2
Pu 239 (instead of 3)

8) Am 241 $\Delta$ = 1
Cm 242 (instead of 3)

Thus, of the two striking lower anomalies in Fig. 4, associated with Ni and Pu, the latter is found to be degenerate as its position in the system is above that of gallium. The only true lower anomaly, i.e., an anomaly that is reflected in the succession of element weights, is the well-known series:

Co 58.940 $\Delta$ = -0.25
Ni 58.690 (instead of +1)

Its establishment is facilitated by its position below gallium, as well as by the fact that Co and Ni lie on the isodifference portion of the curve. In the sections of the curves where the number of excess neutrons increases, the lower anomalies degenerate, of course, much more easily. As the isodifference sectors of the curve are very few in number after gallium, especially between Ag and Cs, the lower anomalies degenerate even more easily. The differences of the element weights drop, to be sure, from 5 to 3 and 2 units, but this is still far from zero and even more so from negative values.

Turning our attention to the upper anomalies, we see that in this case the unfavorable portion of the system will be, as it happens, the beginning (up to gallium), while after the perissad and artiad curves intersect, in the region where the artiad curve lies above the other, every upward shift from this curve may develop into a true anomaly.

An instance corroborating what has just been said is seen in titanium, lying below gallium on the unfavorable section of the curve, i.e., not on an isodifference line; in fact, although there is a rise from $_{46}$Ti to $_{48}$Ti, the mass of vanadium $_{51}$V still exceeds that of $_{48}$Ti: the anomaly is a degenerate one. The reason for this is the excessively large difference in mass between $_{46}$Ti and $_{51}$V -- all of 5 units. The $_{9}$Be - $_{11}$B and $_{4}$He - $_{7}$Li anomalies are likewise degenerate.

Matters are otherwise in the case of argon: to begin with, argon lies on an isodifference line with potassium, and hence the difference between $_{38}$Ar and $_{39}$K is not 5, but only 3 units; moreover, there is an upward shift from $_{36}$Ar to $_{40}$Ar, i.e., of four units, instead of two as in the case of titanium. As a result, we have a classical upper anomaly, which is not annulled by the small admixture of the heavy $_{41}$K.

Ar 39.944 $\Delta$ = -0.848
K 39.096 (instead of +3)

Above gallium, conditions are favorable for the establishment of real upper anomalies, but they may still degenerate; we have an instance of this sort in the Se - Br pair. Here the major isotope $_{78}$Se is only 1 unit smaller than $_{79}$Br; it would seem that the transition from $_{78}$Se to $_{80}$Se warrants the formation of a true anomaly, but this is hampered by the heavy isotope $_{81}$Br (present in almost the same percentage as $_{79}$Br), and what we get is a degenerate anomaly. The rise in weight from Se to Br remains normal.

Se 78.960
$\Delta$ = 0.956
Br 79.916

Matters are otherwise in the case of the analogous pair in the subsequent long period:

Te 127.61 $\Delta$ = -0.69
I 126.92 (instead of +1).

Here the expected major isotope $_{128}$Te is again one unit lighter than $_{127}$I, but the upward shift is not two units, but four, and the heavy isotope of iodine is unstable.

At the end of the system we again have two artiad upward shifts:

230 Th ⟶ 232 Th
236 U ⟶ 238 U

As both of these lie above gallium, and Pa and Np have no long-lived heavy isotopes alongside the normal $_{231}$Pa and $_{237}$Np, two more true anomalies easily develop:

Th 232.12 Δ = −1.12
Pa 231 (instead of +1);
U 238.07 Δ = −1.07
Np 237 (instead of +1)

These anomalies are not strikingly evident in Fig. 4, since Th lies on an isodifference line, and its excess weight over that of Pa ought to be 4; the upward shift from $_{230}$Th to $_{232}$Th makes this difference approximately 6, but there are many such differences in the graph, generally due not to anomalies, but merely to the normal increase in the number of excess neutrons.

The uranium anomaly is likewise concealed in Fig. 4. Although U does not lie on the isodifference line, the anomalous heavy thorium is ahead of it; that is why the increase in weight totals only 6 units.

In spite of such small increases, anomalies do exist -- this again indicates how favorable the region of the system that lies above gallium is to the appearance of upper anomalies.

Thus we have made some progress in our understanding of the so-called anomalies of element weights. We have shown that they depend principally on the singular behavior of the artiad elements, although other factors may, of course, affect degenerate anomalies -- such as the presence or absence of a heavy isotope in the perissad pleiad of the corresponding component of the pair (the case of selenium and bromine). We classed anomalies into two groups according to their genesis: the upper anomalies, the first member of which was the upward shifted artiad (Ar – K, Te – I, Th – Pa, and U – Np); and the lower anomalies, in which the downward shifting artiad is the second member of the pair (Co – Ni). We indicated a number of degenerate anomalies, which no one apparently suspected up to now, and developed the circumstances of the favorable conditions for the degeneration of upper anomalies (He – Li, Be – B, and Ti – V) in the region up to gallium, and the degeneration of eight lower anomalies in the region above gallium (Yt – Zr, Or – Nd, Ho – Er, Ta – W, Ir – Pt, Au – Hg, Np – Pu, and Am – Cm).

The fundamental problem still unexplained in the present paper is that of the genesis of upward and downward shifts of the artiad elements; the problem of the magnitude of the shifts and of their distribution throughout the periodic system. A discussion of these points will be published in forthcoming issues.

In conclusion, we should like to note that there may, of course, be considerable doubt in the group as to our conclusion, and there the suspicion may exist that the existence of the Ar – K anomaly is accidental and not regular. There is reason to assume that this anomaly is not a general occurrence throughout the universe, but only on the earth, owing to the age of the planet and the accumulation of $_{40}$Ar as result of the disintegration of $_{40}$K. The primordial argon of our planet no doubt had a much lower element weight than 39.944.

Received May 15, 1948.

Note: "Element Weight as a Periodic Function. A study of Binary Elements" appeared in the January 1949 issue of the Journ. Gen Chem. (USSR) Pages 1 – 14 of Consultants Bureau English translation. Fig. 4, referred to in the above paper, is evidently Fig. 4 of 'Element Weight as a Periodic Fuontion'. --Consultants Bureau.

# THE ISONUCLEON RULE AND THE APPORTIONMENT OF THE STABLE SUBELEMENTS BETWEEN THE ARTIADS AND THE PERISSADS*

S. A. SHCHUKAREV

It is known that of the total of 273 stable subelements discovered up to the present time only one-fifth, viz.: 55, belong to the perissads, that is, elements whose atomic number is odd, whereas the other 218 belong to the artiads.

To elucidate this relationship, let us construct graph 1, plotting the number of nuclear protons P along the axis of abscissas, and the difference between the number of neutrons and protons, N - P, along the axis of ordinates. All the stable odd and even atoms are indicated on the graph by dots and crosses, the principal isotopes of each element being also denoted by circles.

Each horizontal line on Graph 1 is the locus of points with identical differences N - P i.e., it represents an isodifference line.

We shall renumber the isodifference lines, letting each number equal the corresponding value of N - P, i.e., the number of excess neutrons.

The stable subelements are arranged in a field extending from the isodifference line 1 to isodifference line 44. If the zero isodifference line is counted as even, we have 23 even isodifference lines and 22 uneven ones in this field. On the even isodifference lines we find nothing but even atoms (atoms with an even number of nucleons, or atoms of even mass, as we usually say); on the odd isodifference lines, on the contrary, only uneven atoms are found. The reason for this is plain. At bottom, the even isodifference line corresponds to atoms for which N - P is expressed by an even number; in other words, the number of excess neutrons in the nuclei of these atoms is even and the remaining neutrons are equal in number, of course, to the protons. No matter whether P is even or odd, when it is combined with an identical number of neutrons the sum is even. And if an even number of excess neutrons is added to this even sum, the aggregate sum is even. In other words, when N - P is even, N + P must also be even. It may be similarly shown that when N - P is odd, N + P must also be odd.

It is obvious that the correct distribution of odd and even atoms on the odd and even isodifference lines is inevitable and has only an arithmetical meaning.

Another circumstance is much more complex in its nature and more interesting at bottom, viz.: the fact that when N - P is even, P is even in the overwhelming majority of cases (there are only 4 exceptions: $_{2}H^{1}$, $_{3}Li^{6}$, $_{10}B^{5}$, and $_{14}N^{7}$); i.e., almost all the atoms on the even isodifference lines are artiad atoms (162 artiad and 4 perissad atoms).

This fact is reflected in the graph by the crosses being separated from each other on the even isodifference lines by spaces that correspond to odd abscissas.

As for the odd isodifference lines, the situation is different there: odd values of N - P correspond to even as well as uneven values of P. The dots representing stable atoms almost always lie close together on them, without intervals, i.e., the stable artiad and

* Read before a scientific meeting of Leningrad State University on January 9, 1947.

perissad atoms are all equal, so to speak, on the odd isodifference lines. In fact, of the 107 different stable odd atoms, 56 are artiads and 51 perissads, i.e., they are nearly 50-50.

The spaces* in the solidly filled sections of the odd isodifference lines in the system of stable nuclei are very few in number; they are all listed in Table 1. With regard to this singular distribution of even and uneven atoms among the perissad and artiad pleiads, the view was long ago expressed that the question boiled down to considerations of energy, with the stability of the nucleus depending on whether N and P were even or odd. In general, the atoms that are most stable and most widely distributed in nature are those in which both N and P, and hence the element weight as well, are even numbers; these are the so-called doubly even artiad atoms; there are 162 in all of these stable atoms. The uneven artiad atoms (N odd, P even) are somewhat less stable; there are 56 of them in the stable list. Then there are the uneven perissad nuclei (N even, P odd); there are 51 of these on the stable list. Finally, the least stable, i.e., in most cases radioactive, are the even perissad nuclei (N odd, P even); there are only 4 of these that are stable.

These considerations provide no indication, however, of the origin of these numbers: 162, 56, 51, and 4, although we are at once struck by the fact that the second and third of them are approximately equal, the first is about three times as large, and the fourth approaches zero. To shed light on this problem, let us first examine the two isonucleon (isobar) rules, discovered by the author as long ago as 1922 and published in 1924 [1], but generally known as the isobar principles of Mattuch [2], who discovered them, to the best of our knowledge, ten years later.

TABLE 1

| No. of the isodifference line | | | | |
|---|---|---|---|---|
| 1 | $_{37}Ar^{18}$ | | | |
| 3 | $_{39}Ar^{18}$ | | | |
| 13 | $_{99}Tc^{43}$ | | | |
| 23 | $_{137}La^{57}$ | + $_{139}Ce^{58}$ | | |
| 25 | | $_{141}Ce^{58}$ | $_{143}Pr^{59}$ | $_{147}Pm^{61}$ |

The first rule applies to both perissad and artiad nuclei with an odd number of nucleons; it reads as follows:

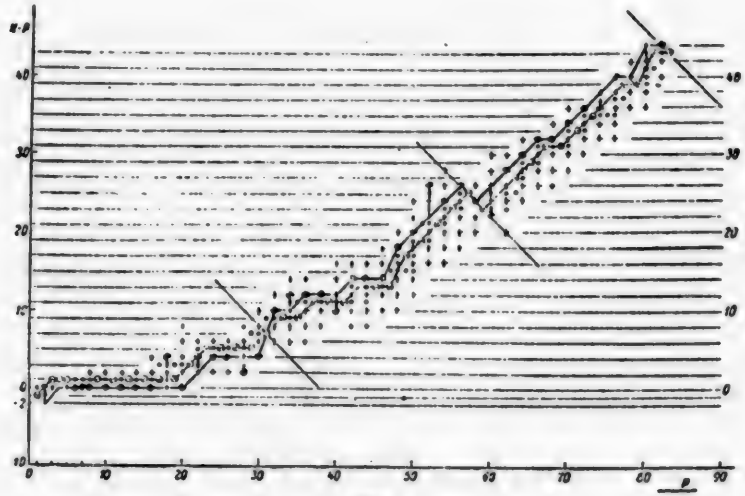
If some "approximately isobaric" or, more precisely, isonucleonic odd nuclei of various elements are encountered in a region of the system where there are stable nuclei, only one of them will almost always be found to be stable (only 4 exceptions are known of the aggregate total of 104 cases); the others are radioactive and are transformed in their nuclei to the sole stable type for the given isonucleon. In other words, the only stable odd isonucleonic atoms encountered in the system are rare exceptions.

To illustrate this rule, we have plotted Graph 2, in which the uneven stable atoms are denoted by little circles, and the uneven radioactive atoms by dots. The principal atoms are represented by double circles, and in the case of radioactive elements by large black circles. The isonucleons are shown as sloping lines, the arrows indicate the direction of the radioactive transformations.

When we examine the graph, we note that 264 radioactive varieties of odd elements, in addition to 107 stable ones, appear; thus there are many instances of chains of isonucleon atoms. For example, there are five different atoms on the isonucleon 49: $_{49}Ca$, $_{49}Sc$, $_{49}Ti$, $_{49}V$, $_{49}Cr$; there are eight atoms on the isonucleon 97: $_{97}Kr$, $_{97}Rb$, $_{97}Sr$, $_{97}Yt$, $_{97}Zr$, $_{97}Nb$, $_{97}Mo$, and $_{97}Tc$; and there are likewise eight atoms on isonucleon 145: $_{145}X$, $_{145}Cs$, $_{145}Ba$, $_{145}La$, $_{145}Ce$, $_{145}Pr$, $_{145}Nd$,** and $_{146}Sm$. Moreover, in each case only one of the isonucleonic

* Cf. another paper "Missing Perissads and Artiads that have no Stable Odd Subelements", p. of this issue.

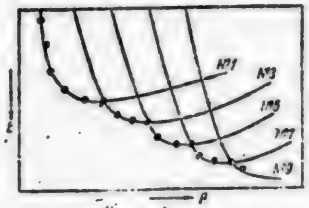
** If $_{145}Pm$ is discovered, it is quite likely that the chain will be filled in with a ninth link.



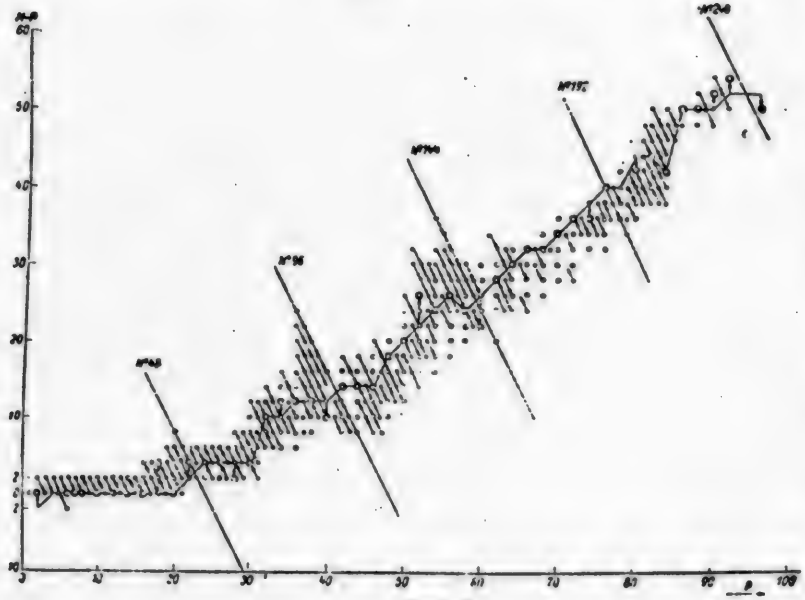
Graph 1

Table 2

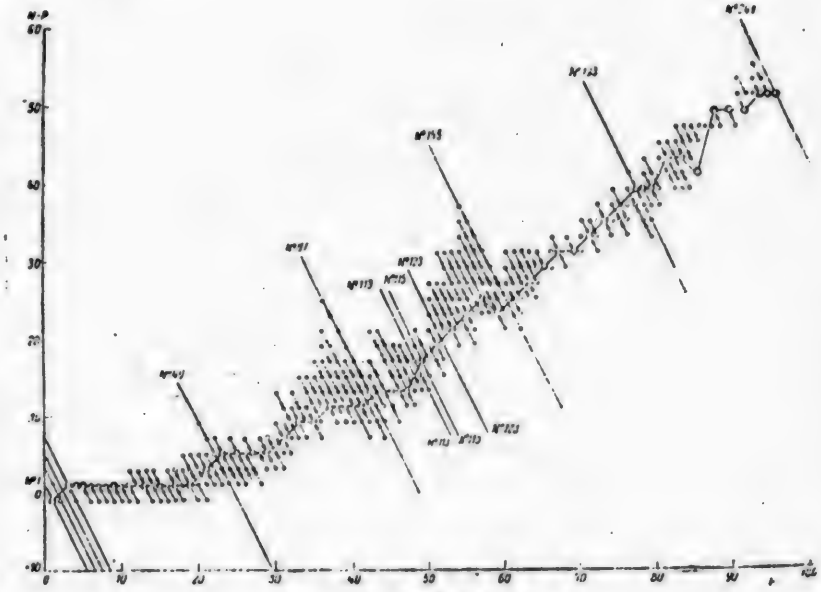
| | $_{18}Ar^{39}$ | $_{19}K^{40}$ | $_{20}Ca^{41}$ | $_{21}Sc^{44}$ | $_{22}Ti^{44}$ | $_{23}V^{49}$ | $_{24}Cr^{51}$ | $_{25}Mn^{54}$ | $_{26}Fe^{59}$ | $_{27}Co^{60}$ | $_{28}Ni^{59}$ | $_{29}Cu^{64}$ | $_{30}Zn^{65}$ | $_{31}Ga^{68}$ | $_{32}Ge^{71}$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | $\beta^-$ | $\beta^-$ | $\beta^-$ | $\beta^-$ | stable | stable | stable | stable | stable | stable | stable | stable | Kap[4] | K | |
| | 110 мин. | 18 мин. | 180 days | 63 часа | | | | | | | | | 250 days | 83 hours | ~165 days |
| | | | | | 5,51% | 100% | 9,43 | 100% | 2,11% | 10,2% | 1,2% | 70,13% | | | |
| Clark of the stable isotope | | | | | 0,034 | 0,02 | 0,0028 | 0,10 | 0,089 | 0,002 | 0,00024 | 0,070 | | | |



Graph 3



Graph 2



Graph 4

atoms in the whole series is stable, viz.: $_{49}Ti$, $_{97}Mo$, and $_{145}Nd$.*

Four isonucleons constitute exceptions: Nos. 113, 115, 123, and 187. Here we encounter not one stable even subelement, but pairs of them, the second always being less effective: $_{113}Cd^{48}$ and $_{113}In^{49}$; $_{115}In^{49}$ and $_{115}Sn^{50}$; $_{123}Sn^{51}$ and $_{123}Te^{52}$; and $_{187}Re^{75}$ and $_{187}Os^{76}$. These pairs of stable isonucleons of a special type are composed of elements that are neighbors in the system, i.e., that possess a $\Delta p = 1$.

Only one of the isonucleons, No. 5, does not correspond to any of the stable atoms.

Let us take three isonucleonic atoms as examples of the application of the first rule:

| | |
|---|---|
| $_{45}Ca^{20}$ | isodifference line No. 5 |
| $_{45}Sc^{21}$ | isodifference line No. 3 |
| $_{45}Ti^{22}$ | isodifference line No. 1. |

These atoms lie on the same isonucleon 45 and on different (and what is more, adjacent) isodifference lines. In accordance with our rule, only one of these nuclei is stable, viz.: $_{45}Sc^{21}$, which possesses the minimum mass and energy; $_{45}Ca^{20}$ and $_{45}Ti^{22}$ are radioactive and are transformed exothermally into $_{45}Sc^{21}$ -- the former by ejecting an electron, and the latter by ejecting a positron, as is indicated in Graph 2 by two arrows pointing toward $_{45}Sc$ from either side.

It should be noted that the average stable form of an isonucleonic nucleus need by no means be an odd perissad atom, as was the case in the example just cited. An odd artiad nucleus may also be stable, as for instance:

| | |
|---|---|
| $_{43}K^{19}$ | isodifference line No. 5, |
| $_{43}Ca^{20}$ | isodifference line No. 3, |
| $_{43}Sc^{21}$ | isodifference line No. 1. |

In this case both the K and the Sc are transformed exothermally from either side into the artiad $_{43}Ca^{20}$.

Thus, in a certain portion of the system, the atoms flow exothermally, as it were, from the isodifference lines 5 and 1 into the fissurelike energy abyss to the isodifference line 3; a number of stable nuclei lie on the latter line, consisting of both perissad and artiad elements:

$$_{35}Cl^{117};\ --^{**};\ _{41}K^{19};\ _{43}Ca^{20};\ _{45}Sc^{21};\ _{47}Ti^{22}.$$

Farther to the left and right along this same isodifference line 3 there lies a series of radioactive nuclei, in turn flowing as it were from this line to the isodifference line 1 (nuclei from $_{40}O$ to $_{38}S$) and to the isodifference line 5 (nuclei from $_{40}V$ to $_{65}Ga$). Generally speaking, it would be well if we could add a third co-ordinate axis to Graph 2, perpendicular to the plane of the figure. On this axis there would be plotted the energies of the various nuclei, both radioactive and stable. Combining the energy values of all the nuclei into a surface as the geometrical locus of the points that characterize the system of atoms from the energy standpoint, we should, of course, have to imagine the main channel of stable isotopes as a sort of deep canyon with steep sides. On these sides there lie chains of electron and positron emitters, exothermally flowing from both sides to the bottom of the canyon. In drawing the cross-section relief of the energy diagram by means of a system of isoproton, isoneutron, isonucleon, and isodifference lines, we would always find, upon following one of these types of iso lines,

* It is also of interest that the three series just referred to, which are the longest of all, differ by the same number of nucleons:

$$1 - 49 - 97 - 145 - (193) - (241).$$
$$\Delta = 48\ \Delta = 48\ \Delta = 48\ \Delta = 48\ \Delta = 48$$

This fact, and the position of the isotope pleiads Ca, Kr, and X in the Mendeleyev system, again remind us of the periodicity mentioned by us in one of our previous papers. In the vicinity of the inert gases the areas of radioactive isotopes shift periodically upward, as it were, together with the abrupt rises of the main channels.

** The reason for the absence of the stable $_{36}Ar^{18}$ between Cl and K will be discussed in a separate paper.

that it first sloped downward -- to the floor of the canyon, i.e., to an energy minimum -- after which it rose, i.e., an endothermic reaction. That is why each of these lines has only one section containing points of stable nuclei, with unstable formation to the left and right of it. All other things being equal, the farther a given nucleus is from the stability section, the less stable it will be.

On the isodifference line 5, for example, we have the following series of nuclei* (Table 2).

When we consider the artiads, to begin with, we note that the series begins with an emitter that has a half-life of 110 minutes, followed by one with a half-life of 180 days; then we have a stable nucleus with a clerk of 0.03%, followed by a clerk of 0.0028 and a clerk of 0.088 The latter value belongs to the most stable artiad nucleus on isodifference line 5, viz.: $_{57}$Fe, lying at the very center of the section of stable nuclei. Iron is followed by Ni with a clerk of 0.00024 and, then by $\beta^+$ emiters with a half-life of 250 days and lastly, of 165 days. Further investigation indicates the probable existence of even more rapidly disintegrating artiads: Si, S, Se, and Kr, on the isodifference line 5.

For the perissads the picture we find is similar: first, $\beta^-$ emitters with half-lives of 18 minutes and 68 hours, then stable V, Mn, Co, Cu with clerks of 0.02, 0.10, 0.002, and 0.070 respectively (Mn is alongside Fe), and, lastly, Fe with a half-life of 83 hours.

The channel of stable nuclei traverses the system of isodifference lines in such a way that the longer or shorter sections of these lines, which determine the system of stable isotopes, all lie in this channel, in the order of increasing atomic number.

Graph 3 shows a schematic picture of the energy competition among the isodifference lines for the right of having one long chain or another of stable perissads within a given range of atomic numbers.

The isodifference lines in Graph 3 intersect one another, and the energy level of the nuclei on two adjoining isodifference lines are identical (approximately) for the abscissa of this intersection, i.e., for a given value of P. In these cases there arise odd doublets of the perissads or artiads, such as, $_{39}$K and $_{41}$K; $_{63}$Cu and $_{65}$Cu; $_{47}$Ti and $_{49}$Ti; $_{95}$Mo and $_{97}$Mo. It is quite essential, of course, to note that odd doublets originate when the main channel moves from one isodifference line to the next (this is seen in Graph 2). As there are 23 odd isodifference lines within the region of stable nuclei, we should expect there are 22 transitions and, hence, 22 odd doublets.

From this it is easy to derive, in the first approximation, the aggregate number of stable odd nuclei, viz.: the number of elements from H to Bi, inclusive, is 82; if 22 of them have odd doublets, and the others are odd singlets, then the overall number of odd stable nuclei will total 105 (44 + 61 = 105).

In fact, this value just computed by us is, as we know, two units smaller than that found experimentally. The number of odd doublets found by experiment is likewise 28 instead of 22.

It should be borne in mind that in one case of transitions from one isodifference line to another there is no doublet, namely, the second member of the doublet $_{3}$He – $_{5}$He, corresponding to the isodifference lines 1 and 3. Thus, the figure 28 exceeds the number of expected doublets, i.e. 21, by 7.

It is apparent from Graph 2 that of these 7 instances, 3 correspond to the doublets $_{113}$In – $_{115}$In; $_{117}$Sn – $_{118}$Sn; and $_{123}$Te – $_{125}$Te, the second members of which are the examples explained above of exceptions to our first isonucleon rule. Thus, the number of expected odd atoms becomes equal to that found experimentally, i.e., 107, since 105 – 1 + 3 = 107. The other four surplus doublets do not affect this figure, as their presence, owing to the effect of our first rule, is compensated by the 4 elements without odd nuclei which are bound up

* A more detailed discussion, similar to the one dealing with Table 2, will be published in a separate paper.

with them*.

| Surplus doublets | Elements without odd nuclei |
|---|---|
| $_{35}Cl - _{37}Cl$ | Ar |
| $_{95}Mo - _{97}Mo$ | Tc |
| $_{135}Ba - _{137}Ba$ | Ce |
| $_{143}Nd - _{145}Nd$ | Pm |

Another, and even simpler method of calculating the number of stable odd nuclei is as follows: In accordance with our first rule, a single stable type of nucleus corresponds to every odd isonucleon; since there are 103 odd numbers between $_1H$ and $_{209}Bi$, there ought to be 105 stable subelements. Moreover, we remember that isonucleon 5 does not correspond to any stable atom; there then remain 104 stable ones; 3 instances of odd isonucleons increase the figure to 107.

It is apparent from Graph 2 that the odd nuclei should be more or less equally distributed between the artiads and the perissads.

The second isonucleon rule applies to artiad, as well as to perissad, even nuclei; it consists of the following:

If there are some isonucleonic nuclei belonging to different elements in the region of stable nuclei, one (43 instances), two (35 instances) and, by way of exception, three (4 instances) of them turn out to be stable. In paired stable isonucleonic nuclei, which is the case that is of greatest interest to us at the moment, both kinds of atoms belong to the neighboring artiad in the system ($\Delta p = 2$) and are located on four isodifference lines that differ in number by 4, i.e., $\Delta(N - P)$. The even perissad nucleus located on the intermediate even isodifference line is radioactive and can be transformed into the indicated stable artiad. This rule has its own well-known energy basis.

We have plotted Graph 4 to illustrate the effect of the second rule; in this graph the circles designate stable even atoms, and the dots denote radioactive even atoms. The major isotopes are denoted by double circles, and if they are radioactive elements, by large black circles. The sloping lines and arrows have the same significance as in Graph 2. The graph indicates that, in addition to 167 stable even subelements, 204 radioactive even ones have been discovered, that is, fewer than the odd radioactive ones, contrary to what might have been expected. Thus, the even subelements total 371, which differs but slightly from the total of odd ones, 368. (107 stable ones and 261 radioactive).

The whole thing boils down to the stable elements constituting some 46% of the total of even subelements, and about 29% of the odd ones.

Not only are the totals of odd and even kinds of atoms fairly close to each other, but the very configuration of the points in Graph 2 resembles that in Graph 4. The peculiar isonucleons 49, 95, and 145 correspond to the similarly peculiar isonucleons 48, 94, and 144.

The principal difference between the two graphs is the distribution of the stable types over the whole field. Whereas Graph 2 constitutes a striking illustration of the first rule, i.e., the trend toward the central channel from above and below, in Graph 4 we see an illustration of the second rule, i.e., a scattering upward and downward from the central channel, a scattering that results in the almost total disappearance of the stable even perissads and in the appearance of numerous pairs of stable isonucleonic atoms.

As a result, besides the singlets (8 instances) and the doublets (4 instances), we have the more complicated isotopic pleiads for the even type of atom (7 triplets of even isotopes, 10 quartets, 13 quintets, 2 sextets, and 2 septets of even isotopes).

Let us take three isonucleonic atoms as an example of the application of the second rule:

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* See the following paper for details.

| | |
|---|---|
| $_{40}Ar^{18}$ | isodifference line 4 |
| $_{40}K^{19}$ | isodifference line 2 |
| $_{40}Ca^{20}$ | isodifference line 0 |

According to the rule, the atoms of the even perissad $_{40}K^{19}$ ought to be unstable, transforming into the artiad atom $_{40}Ar^{18}$ by ejecting a positron and transforming into the artiad atom $_{40}Ca^{20}$ by ejecting an electron, which is what actually happens. The following dual disintegrations are other examples: $_{36}Cl^{17}$; $_{46}Sc^{21}$; $_{64}Cu^{29}$; $_{74}As^{33}$; $_{76}As^{33}$; $_{102}Rh^{45}$; $_{112}In^{49}$; $_{152}Eu^{63}$. It may be expected that an even larger number of such cases will eventually be discovered.

Thus, while sections are formed on the uneven isodifference lines, uninterruptedly filled with perissad, as well as artiad, uneven atoms that correspond to successive values of P (without a gap in the even or odd numbers), on the even isodifference lines there are only the nuclei that correspond to even values of P; the perissad points (uneven P) on the even isodifference lines remain unfilled in the system of stable nuclei, in accordance with our second rule.

When even perissad nuclei of the main channel are transformed into artiad nuclei that are isonucleonic with them, the atoms are ejected, as it were, into the adjoining channels, usually forming in these channels stable, and sometimes major, isotopes of the respective elements.

Thus, for example, the even perissads of the isodifference line 0 become radioactive after $_{14}N^{7}$, i.e., beginning with $_{18}F^{9}$: all of them on the isodifference line 2 correspond to the following stable subelements.

| | | | | | | |
|---|---|---|---|---|---|---|
| $_{18}O^{8}$ | $_{22}Ne^{10}$ | $_{26}Mg^{12}$ | $_{30}Si^{14}$ | $_{34}S^{16}$ | $_{38}Ar^{18}$ | $_{42}Ca^{20}$ |
| 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| ↑ | ↑ | ↑ | ↑ | ↑ | ↑ | ↑ |
| $_{18}F^{9}$ | $_{22}Na^{11}$ | $_{26}Al^{13}$ | $_{30}P^{15}$ | $_{34}Cl^{17}$ | $_{38}K^{19}$ | $_{42}Sc^{21}$ |

In connection with the radioactivity of the even perissads investigated by us, the section of the isodifference line 0 in the system of stable nuclei looks like this:

$$_{16}O^{8} - _{20}Ne^{10} - _{24}Mg^{12} - _{28}Si^{14} - _{32}S^{16} - _{36}Ar^{18} - _{40}Ca^{20}$$

In accordance with what has been asserted in one of our previous papers, the main channel of odd nuclei was drawn by us through the main isotopes of the perissads (with the sole exception of nitrogen), the main channel of the even nuclei being subordinated conventionally to the odd one, i.e., it was drawn parallel to it (with the fundamental exception of the single point of intersection). The main channel of the even nuclei might have been drawn through the main isotopes of the artiads, considering it as possessing its own configuration. We preferred to proceed otherwise, holding that the two channels are, in principle, parallel and endeavoring to explain their discrepancies as due to upward and downward artiad shifts, originating in our second rule.

In the interval from $He^{2}$ to $Pb^{82}$ there are 81 elements in all: 41 artiads and 40 perissads. Our conventional main channel of even nuclei is such that all the 81 elements cannot be accomodated in it along thin stretch, since at its inclined sections it intersects many abscissas with odd ordinates. We come up against this fact in Graph 4 for 19 perissads* (Li, Sc, V, Ga, Br, Nb, In, Sb, Cs, La, Pr, Pm, Eu, Tb, Tm, Lu, Ta, Re), along the inclined sections of the channel. The other 21 perissads (B, N, F, Al, P, Cl, K, Mn, Co, Cu, As, Rb, Yt, Te, Rh, Ag, Ho, Ir, Au, Tb) correspond to the main channel for even mass numbers, i.e.,

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* An analogous circumstance is encountered in Graph 2 for 20 artiads (He, Ca, Ti, Zn, Ge, Kr, Mo, Sn, Te, X, Ba, Ce, Nd, Sm, Gd, Dy, Yb, Hf, W, Os).

generally practicable; of these, only $_{10}B$ and $_{14}N$ are stable, the other 19;* subject to the second rule, are all transformed into stable artiads.

In our conventional main channel, the artiad abscissas correspond to even isodifference lines, i.e., even atoms; not all of them, however, correspond to the main isotopes of the respective elements, only 28 (C, O, Ne, Mg, Si, S, Ca, Cr, Fe, Zn, Ge, Kr, Sr, Mo, Ru, Pd, Cd, Sn, X, Ba, Ce, Sm, Gd, Dy, Yb, Hf, Os, Pb) doing so; the other 13 of the main artiads of the subelements originate, at bottom, in accordance with the second rule, either above (6 cases) or below (7 cases) the main channel.

The following elements: Ni, Zr, Nd, Er, W, Pt and Hg have their own major isotopes below the main channel. In three of these instances ** we are dealing with a quite simple phenomenon, namely, the electronic transformation of an even perissad of the main channel into a main even artiad lying below the channel:

The other 16 even perissads of the main channel yield, upon transformation, not the main, but secondary stable subelements.

In this paper we shall not touch upon the origin of the other lower main artiads: $_{142}Nd$, $_{184}W$, $_{202}Hg$ and upper main artiads $_{4}He$, $_{40}Ar$, $_{48}Ti$, $_{80}Se$, $_{130}Te$; this is more complicated, involving the transformation of the even perissads of auxilliary channels, and not of the main channel. The origin of the main odd artiads $_{196}Pt$ and $_{9}Be$ will also be ignored for the time being. As for the overall number of stable even atoms (166), this may be explained as follows, as was done above for the odd atoms.

In the region from $_{2}He^{4}$ to $_{208}Pb^{82}$ there are 104 even numbers in all. One of them, namely eight, proves to be unstable, as $_{8}Li^{8}$ is transformed into $_{8}Be^{4}$, the latter breaking down into two $\alpha$-particles, this occurring so rapidly that it is extremely difficult to observe the very existence of this kind of beryllium. Thus, there are 103 even numbers left, which may be assumed to have been originally more or less uniformly distributed between the artiad and perissad abscissas. Furthermore, it may be quite schematically supposed that if all, i.e., some 50, of the even perissads were to disintegrate in accordance with the second rule, each giving rise to a pair of stable even artiads, the number of even artiads would attain a figure of the order of 150 (this figure actually is 162). Lastly, the multiplication of artiad subelements is a more complicated affair, of course, even though the scheme set forth above does have a meaning in principle.

Diagram of the Distribution of Stable Subelements

| Number of subelements | | |
|---|---|---|
| With even mass numbers | With odd mass numbers | Total |
| 50 perissads | (50) | 50 |
| 50 artiads | 50 50 50 | 200 |

It is evident from the diagram that there should be about four times as many stable artiads as stable perissads, and about one fourth of the artiad subelements should be uneven; this is actually the case.

* One species of the 19, namely $_{100}Te^{43}$, has not been discovered as yet, but it is doubtless radioactive, changing into the stable $_{100}Mo$.

** The conversion of $_{58}Co^{27}$ into $_{58}Ni^{28}$ has not been demonstrated experimentally as yet.

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# MISSING PERISSADS AND ARTIADS THAT HAVE NO STABLE ODD SUBELEMENTS*

S. A. SHCHUKAREV

As we know, several elements remained undiscovered for some time: the perissads 43, 61, 85, and 87. As for the last two, astatine and francium, the problem was solved naturally, after the discovery of the fourth radioactive family of unstable atoms with masses of the type $4n + 1$, i.e., the neptunides. The first two, technetium and prometheum, likewise produced artificially now, attract our attention because, though located in the system's region of stable elements, neither has any stable isotopes.

It is the aim of the present paper to show that this is not fortuitous, having its analogues in the isotope pleiads of argon and cerium, which no one has as yet observed, as far as we know.

Argon and cerium are even-numbered (18 and 58), i.e., they are artiads and, hence, differ from the perissads in that most of their stable isotopes ought to be even, which is actually the case:

$$_{36}Ar,\ _{38}Ar,\ _{40}Ar;\quad _{136}Ce,\ _{138}Ce,\ _{140}Ce,\ _{142}Ce.$$

It is striking, however, that, in contradistinction to all other artiads, not a single stable odd isotope has yet been found for either argon or cerium. What is more, we have become accustomed to the presence of traces of odd atoms (one or two species) serving as an unfailing attribute of every artiad; in fact, of the 41 artiads that possess stable subelements, 39 have odd atoms among their obligatory ingredients.

It might be thought that the absence of stable odd atoms in the pleiads of argon and cerium is the result of incomplete research, and that this shortcoming will be eliminated with the passing of time. We assert, however, that the occurrence in nature or the artificial production of stable odd atoms of argon and cerium is as unlikely as the occurrence of stable atoms of technetium and prometheum, since the reason for their absence is the same in both cases. Besides, it is obvious to us that the artiads that have no stable odd subelements ought to exist in about the same proportions as the "missing perissads".

In the paper entitled "The Isonucleon Rule and the Apportionment of the Stable Subelements Between the Artiads and the Perissads" we demonstrated that the odd subelements of the perissads and artiads constitute one overall system, subject to the same first isonucleon rule. The single channel of stable odd subelements crosses the odd and even abscissas, giving rise to approximately the same number of odd perissads and even artiads, but only rarely giving rise to the same phenomenon for both of them — the disappearance of the stable atoms. If this sort of disappearance occurs in a perissad, the element vanishes altogether as a stable phenomenon of nature, since it has no other, that is, even, stable atoms. If this disappearance takes place in an artiad, the element does not vanish, as it still has available even atoms, but it becomes an artiad without any stable subelements.

Graph 1 shows the place in the system where the transitions from isodifference lines 1 to 3 and 3 to 5 take place.

The latter transition takes place simply, i.e., at the same abscissa 22 where a number of stable nuclei of isodifference line 3 terminate in $_{47}Ti$, and a number of stable nuclei of the isodifference line 5 begin at $_{48}Ti$; as a result, the odd doublet $_{47}Ti$ — $_{49}Ti$ originates in the pleiad of titanium.

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* Read at a meeting of the Leningrad Section of the D. I. Mendeleyev All-Union Chemical Society on March 25, 1948.

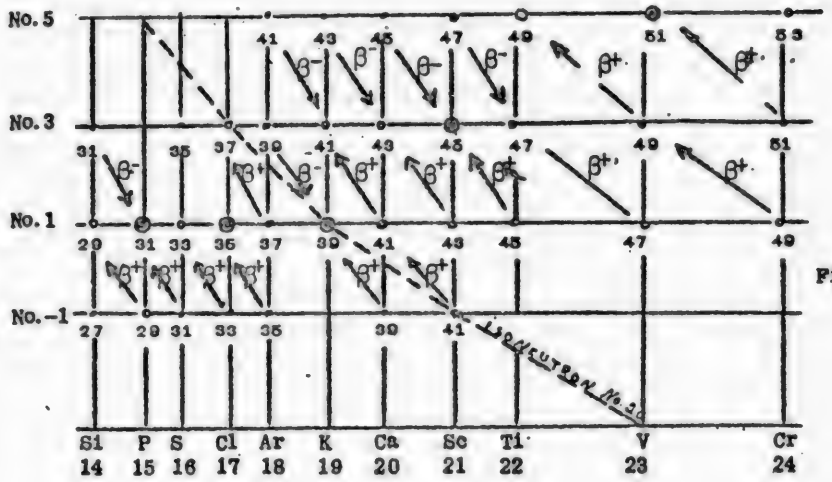


Fig. 1.

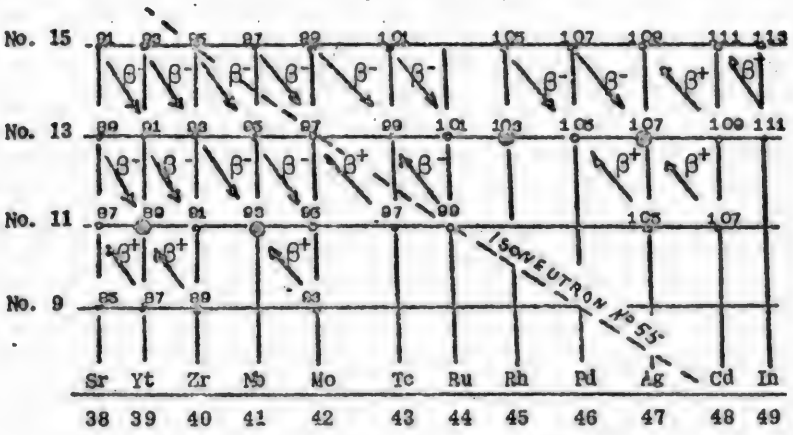


Fig. 2.

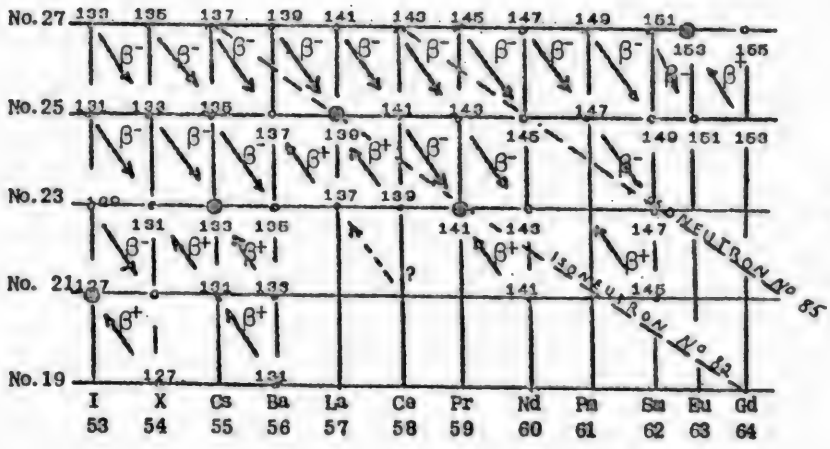


Fig. 3.

The transition from the isodifference line 1 to the isodifference line 3 is marked by the appearance of not one, but two doublets: $_{35}Cl$ — $_{37}Cl$ and $_{39}K$ — $_{41}K$. This circumstance likewise leads to the odd isotopes of argon dropping out of the system of stable isotopes.

At bottom, argon could have stable odd isotopes either on isodifference line 1, namely, $_{37}Ar$, or on isodifference line 3, namely, $_{39}Ar$. In agreement with the first isonucleon rule, the existence of the stable atoms $_{37}Cl$ and $_{39}K$, eliminates both of these species of argon from the list of stable species. In fact, $_{39}Ar$ turns out to be an emitter of $\beta^-$ with a half-life of 4 minutes, whereas $_{37}Ar$ is a $\beta^+$ emitter with a half-life of 34 days. The presence of the stable $_{37}Cl$ and $_{39}K$, which both lie on the same isoneutron line 20, is essential for the instability of both of the odd isotopes of argon, which might otherwise claim the role of stable atoms.

When we turn to technetium, we see a picture that is quite similar (Graph 2).

Here, as in the previous example, the transition from the isodifference line 13 to the isodifference line 15 is a simple one, signalized by the appearance of one odd doublet of the stable isotopes of silver, $_{107}Ag^{47}$ — $_{109}Ag^{47}$. The transition from the isodifference line 11 to line 13, like the earlier one from line 1 to line 3, is three atomic numbers to the left of the doublet $_{107}Ag$ — $_{109}Ag$ and consists of two doublets: $_{95}Mo$ —$_{97}Mo$ and $_{99}Ru$ — $_{101}Ru$. Since the stable atoms $_{97}Mo$ and $_{101}Ru$ are isoneutron (on isonuetron 55), both of them lay claim to stability; $_{97}Tc$ and $_{99}Tc$ become radioactive (half-life of the first = 95 days; half-life of the second = 40 years), and element Tc falls into the category of missing perissads. It is typical that the masses of the Ti and Ag doublets differ from each other by 60 units, i.e., by the same amount as the masses of the Ar and Tc atoms that lost their stability

In general, the surroundings of the Ar and Tc unstable doublets resemble each other; they constitute a sort of periodic phenomenon in the system, with a displacement interval of 10 numbers in the system of the isodifference lines, of 25 numbers (43-17) in the isoproton system, of 35 numbers in the isoneutron system (55-20), and of 60 units in the isonucleon system (97-37; 99-39; 107-47, etc.).

The third and fourth instances of the loss of stable odd isotopes both lie on the transition from the isodifference line 23 to the isodifference line 25, and hence it will be convenient to consider them together (Graph 3).

We see from Graph 3 that the transition from isodifference line 21 to isodifference line 23, as well as the transition from line 25 to line 27 take place simply via the appearance of the doublets $_{129}X$ — $_{131}X$ and $_{151}Eu$ —$_{153}Eu$.

The transition from isodifference line 23 to isodifference line 25 is much more complicated. Here there are two isoneutron pairs of stable atoms: $_{139}La$ and $_{141}Pr$ on isoneutron line 82, and $_{145}Nd$ and $_{147}Sm$ on the isoneutron line 85. The second isoneutron pair is the result of the existence of the two stable doublets: $_{145}Nd$ — $_{145}Nd$ and $_{147}Sm$ — $_{149}Sm$, which, in accordance with the first rule, make it impossible for the isotopes $_{145}Pm^{61}$ and $_{147}Pm^{61}$ to be stable. The first of these isotopes of prometheum has not been adequately investigated as yet, though it is probably formed in the transformation of $_{145}Sm$ and must itself be rapidly transformed into $_{145}Nd$. The second of these claimants to stability: $_{147}Pm$, has been produced artificially, but it is transformed rather rapidly (half-life of 3.7 years) into $_{147}Sm$.

It is of interest that $_{145}Pm^{61}$ is 48 nucleons and 18 protons away from $_{97}Tc^{43}$, reminding us of the periodicity of the long periods of D. I. Mendeleyev's system.

Moreover, the isonucleon lines 97 and 145 are both distinguished for the length of their radioactive chains, and both begin with the inert gases Kr and X, as was pointed out in our previous paper.

The isoneutron pair $_{139}La$ —$_{141}Pr$, which exclude the stability of the odd isotopes of

cerium, $_{141}Ce$ (half-life of 30 days), and $_{139}Ce$ (half-life of 2.1 minutes), is of quite singular origin.

Here there are not two stable doublets, as in the cases of Ar, Te, and Pm, there being a hiatus in the long isodifference series of stable atoms (on isodifference line 23): $_{137}La$ and $_{138}Ce$ become unstable, being transformed into the stable $_{137}Ba$ and $_{139}La$; thus, stable atoms appear on the isodifference line 25 prematurely as it were, before the final transition to it.

This phenomenon should be linked up with the special significance of the isoneutron line 82,* as well as with the circumstance that in the second half of the system (beginning with $Ag^{47}$) we observe the general tendency toward a rapid rise from one isodifference line to another without long delays as expressed in horizontal series of isodifference stable atoms. Between the isodifference lines 23 and 25 we observe a sort of struggle between two tendencies: forming a horizontal row or rising to the next stage.

As result the second "missing perissad" — prometheum — and the second artiad that has no stable odd isotopes — cerium — make their appearance.

It is interesting that the technetium anomaly, analogous to the prometheum anomaly, is accompanied by a hint, as it were, of a possible second anomaly, similar to that of cerium. As a matter of fact, it is known that the stable $_{85}Rb$, lying on the isodifference line 11 is followed by the radioactive $_{87}Rb$ on the isodifference line 13, with an extremely long half-life of $6.3 \times 10^{10}$ years. In this fact we may see the marked tendency toward the premature transition to the isodifference line 13, analogous to the transition of barium and lanthanum from line 21 to line 23. If $_{87}Rb$ were fully stable, this would entail the instability of $_{87}Sr$ according to our first rule, and then strontium, like cerium and argon, would be deprived of their last stable odd isotope.

Thus, if we bear in mind the fact that although no anomaly of strontium has yet manifested itself, it nevertheless should exist, there are 5 peculiar points in all in the system with expressed or clearly projected tendencies toward the disappearance of the stability of odd atoms:

$$Ar^{18} \frac{\Delta P = 20}{} (Sr^{38}) \frac{\Delta P = 20}{} Ce^{58}, \qquad Te^{43} \frac{}{\Delta P = 18} Pm^{61}.$$

Hence, the absence of stable odd isotopes of argon and cerium is by no means accidental, being due to the same cause as the absence of stable isotopes of technetium and prometheum.

* Cf. the foregoing article in this issue of the Journal of General Chemistry.

Received
December 28, 1948.

# A NEW WAY OF REPRESENTING THE D. I. MENDELEYEV SYSTEM OF ELEMENTS

A. P. PAUSTOV

The author proposes the following arrangement of the elements in the periodic system (cf. Table) in order to eliminate the present defects in the Mendeleyev system related to the wrong position of the lanthanoids, the actinoids, part of the elements in Group VIII, etc.

| PERIODS | Groups of elements | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | I | II | III | IV | V | VI | VII | VIII | IX | X |
| | 1 2 3 | 1 2 3 | 1 2 3 | 1 2 3 | 1 2 3 | 1 2 3 | 1 2 3 | 1 2 3 | 1 2 3 | 1 2 3 |
| 1 | H | He | | | | | | | | |
| 2 | Li | Be | B | C | N | O | F | Ne | | |
| 3 | Na | Mg | Al | Si | P | S | Cl | Ar | | |
| 4 | K | Ca | Sc | Ti | V | Cr | Mn | Fe | Co | Ni |
| | Cu | Zn | Ga | Ge | As | Se | Br | Kr | | |
| 5 | Rb | Sr | Y | Zr | Nb | Mo | Tc | Ru | Rh | Pd |
| | Ag | Cd | In | Sn | Sb | Te | I | Xe | | |
| 6 | Cs | Ba | La | Ce | Pr | Nd | Cy | | | |
| | Sm | Eu | Gd | Tb | Dy | Ho | Er | | | |
| | Tu | Yb | Cp | Hf | Ta | W | Re | Os | Ir | Pt |
| | Au | Hg | Tl | Pb | Bi | Po | At | Rn | | |
| 7 | Fr | Ra | Ac | Th | Pa | U | Np | | | |
| | Pu | Am | Cm | | | | | | | |

The Periodic System of the Elements

As shown in the table, each group has 3 subgroups instead of the 2 subgroups now employed.

The first subgroup comprises the elements completing an outer electron shell;

The second subgroup comprises the elements completing the second outer electron shell;

The third subgroup comprises the elements completing the third outer electron shell (the lanthanoids and the actinoids).

The allocation of the elements into groups is effected on the basis of the number of electrons in the three completed electron shells: the external, the second outer and the

third outer shells; in the lanthanoids and the actinoids, both the completely filled as well as the half-filled f-electron subgroups (14 and 7 electrons) are considered to be stable.

The correspondence between the number of 6s, 5d, and 4f electrons in the lanthanoids and their sequence number within the group is seen from the following table:

Ce — $4f^2 6s^2$; Pr — $4f^3 6s^2$; Nd — $4f^4 6s^2$; Cy — $4f^5 6s^2$; Sm — $(4f^7 6s^1)$;
Eu — $4f^7 6s^2$; Gd — $4f^7 5d^1 6s^2$; Tb — $4f^{7+2} 6s^2$; Dy — $4f^{7+3} 6s^2$;
Ho — $4f^{7+4} 6s^2$; Er — $4f^{7+5} 6s^2$; Tu — $(4f^{14} 6s^1)$; Yb — $4f^{14} 6s^2$;
Cp — $4f^{14} 5d^1 6s^2$;

It is assumed that in Sm and Tu one s electron shifts into the f position, thus resulting in the structure indicated for them.

The properties of the lanthanoids and the actinoids in so far as they have been investigated, likewise confirm the correctness of the arrangement suggested by us.

Thus, Ce, the first element after La, ought to be placed in Group IV; this may be taken to be established by now. It is similar in its properties to Zr and Hf (and even more closely similar to Th).

Tb has properties that resemble those of Ce. Its place in the periodic table is in Group IV after Ce.

A tendency to exhibit a higher valency than 3 is also observed in the elements that follow after Ce and Tb. Thus, a compound has been reliably established for Pr in which the latter is tetravalent ($PrO_2$). On the basis of their electron structure it may be assumed that Dy, which is a direct analogue of Pr, is also tetravalent.

On the other hand, in the elements of the lanthanoid family that are in Groups I and II in the table set forth above, we find a tendency toward lower valency. Thus, Sm (in Group I) and Eu and Yb (in Group II) enter into compounds in which they are bivalent.

There is every reason to believe that Tu, which is fully analogous to Sm, also tends to be bivalent. It should be borne in mind in this connection that the compounds of bivalent Eu and Yb are more stable than the compounds of bivalent Sm, which fully agrees with their position in Group II. On the other hand, the instability of the compounds of bivalent Sm may be compared to some extent to the instability and singularity of the compounds of bivalent Ag and Au.

It may not be superfluous to note that the properties of the sulfates of Eu and Yb remind us of the properties of the sulfates of the alkaline-earth metals.

Gd and Cp, which are always trivalent, are in Group III and are wholly analogous to each other.

Nor do the properties of the actinoids contradict what is indicated by their arrangement.

As may be seen from the table, Th is a direct analogue of Ce and an indirect analogue of Hf and Zr, which happens to correspond to the greater resemblance between Th and Ce than between Th and Hf and Zr.

Pa and U remain indirect analogues of Ta and W. Thus, Th, Pa, and U do not lose their places in Groups IV, V, and VI, respectively, merely shifting from the second to the third subgroup.

The need for 10 groups instead of the present 9 likewise flows from the following considerations:

If two elements of the first period, completing their electron shell with s electrons, occupy two different groups; if 8 elements of the second and third short periods, completing

their outer electron shells with s and p electrons, constitute 8 groups, then the 18 elements of the long periods (with s, p, and d electrons) must occupy 18 groups (instead of 16 as in the present periodic table). 8 of these elements with s and p electrons are direct analogues of the elements of the short periods and are arranged in the present 8 groups; of the 10 elements with d electrons, 8 fall into the same 8 groups as indirect analogues of the elements of the short periods; and only two: Co — Ni; Rh — Pd; and Ir — Pt, which have no analogues in the short periods, have to form two new groups: 9 and 10.

Thus, if two groups correspond to two elements with s electrons (H and He), and 6 groups correspond to 6 elements with p electrons, then 10 groups (instead of the existing 8) must correspond to 10 elements with d electrons, which fixes the maximum number of groups in the periodic table.

The special nature of Groups 9 and 10 and the absence of analogues in the short periods for elements of these groups are not isolated phenomena in Mendeleyev's periodic table; they also are exhibited in the transition from the first short period, consisting of 2 elements, to the second short period, consisting of 8 elements.

The elements of 6 groups (III, IV, V, VI, VII, and VIII) of the second and third periods have no analogues in the first period, as there are only two s electrons in the two elements of the first period, while the elements of the second and third periods have two s and six p electrons; the difference is $8 - 2 = 6$.

When we compare the elements having s and p electrons with those having d electrons the difference becomes: $10 - 8 = 2$ which fixes the singularity of two groups of elements with d electrons.

With the proposed arrangement of the lanthanoids and actinoids, the horizontal analogy of the elements in the periods among elements with d electrons (first interpolation) and especially among elements with f electrons (second interpolation) is clearly exhibited.

This analogy takes on the character of a rule that is inherent in the Mendeleyev periodic system, similar to the analogies of elements by groups.

In conclusion, we consider it necessary to refine the appelations of the periods by giving them the following names:

a) short periods—the 1st, 2nd, and 3rd, comprising 2, 8, and 8 elements, respectively;

b) medium periods — the 4th and 5th, each comprising 18 elements; and

c) long periods — the 6th, containing 32 elements, and the 7th (incomplete), containing 10 elements.

Received December 15, 1948.

# THE QUANTUM-MECHANICAL REPRESENTATION OF THE PERIODIC SYSTEM OF THE ELEMENTS*

G. M. MURASHOV

The periodic law of D. I. Mendeleyev is a fundamental law of nature, the foundation of modern chemistry.

The present paper represents an endeavor to construct the periodic table of the elements on the basis of a quantum-mechanical interpretation of the periodic law.

Application of the principles of quantum mechanics to the construction of the table makes it possible to furnish a theoretical foundation for the form of the table**, if the elements are arranged according to their quantum numbers in the order of the filling in of their electron levels:

1s, 2s, 2p, 3s, 3p, 4s, 3d, 4p, 5s, 4d, 5p, 6s, 4f, 5d, 6p, 7s, 5f, 6d

and the elements are divided according to the arrangement of the electrons in the atoms into s, p, d, and f elements, respectively.

The classification - systematization and periodization - of chemical elements into subgroups and rows according to the values of the principal and subsidiary quantum numbers on the basis of the Pauli "interdiction" made it possible to represent the periodic system in two variants of the table - the "long" and the "short".

## CONSTRUCTION OF THE TABLE

### Horizontals

1. Periods (seven) -

The distribution of the elements in the system according to the value of their principal quantum number (electron shell): $n = 1 - 7$ and corresponds to the energy levels of the electron in the hydrogenoid atom.

In agreement with this, the length of the periods - the number of elements in each period - is determined by the number of electrons filling the given level and equal to:

$$2 - 8 - 8 - 18 - 18 - 32 - 32.$$

2. Rows (seventeen) -

The distribution of the elements in periods according to the value of the subsidiary quantum number (form of the electron shell): $l = 0 - (n - 1)$ and corresponds to the sequence of filling the electron states (nuclei) in the elements' atoms.

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* Read at the memorial meeting for D. I. Mendeleyev of the Students' Scientific Society of the Faculty of Chemistry of Leningrad University, 14 February, 1948.

** On the basis of modern concepts of the atom it may be stated that the properties of an element: the mass of the atom, the structure and charge of the nucleus, and the structure of its electron shell, are determined by the element's place in Mendeleyev's periodic system of the elements (its atomic number). From this there follow the demands that must be met by the form of the table that graphically depicts the periodic law.

Accordingly, the elements are divided into rows in accordance with the electronic formulas:*

1. (1, 2, 3, 4, 5, 6, 7) s-elements (7 rows of 2 s-elements);
2. (2, 3, 4, 5, 6) p-elements (5 rows of 6 p-elements);
3. (3, 4, 5,) d-elements (3 rows of 10 d-elements);
4. (4,5) f-elements (2 rows of 14 f-elements, one row being incomplete);

or, when the rows are designated by the name of the first element in the respective row:

1. H, Li, Na, K, Rb, Cs, and Fr;
2. B, Al, Ga, In, and Tl;
3. Sc, Y, and Cp (Hf);
4. La, Ac (Ce, Th).

Thus,

The 1st period has one row;
The 2nd and 3rd periods have two rows;
The 4th and 5th periods have three rows;
The 6th and 7th periods have four rows.

## Verticles

1. Groups (four) -
The distribution of the elements in each period according to uniform electron states of the atoms.

Accordingly, the elements - depending on the filling of the levels with electrons — are divided into groups of s-, p-, d-, and f-elements or Groups I, II, III, and IV, each period always starting with an s-element and concluding with a p-element. (See "Long" Table).

2. Subgroups (thirty-two) —
The distribution of the elements in each group according to similar electronic formulas for the outer shells of the unexcited atoms, having the same number of outer electrons in identical states, but at different levels.**

Accordingly, the elements are divided — by the electronic formulas for the atoms — into the following subgroups:

1. Of $s^{1-2}$ elements (2 subgroups, each of 7 s-elements);
2. Of $p^{1-6}$ elements (6 subgroups, each of 5 p-elements);
3. Of $d^{1-10}$ elements (10 subgroups, each of 3 d-elements);
4. Of $f^{1-14}$ elements (14 subgroups, each of 2 f-elements , 7 of which are incomplete);

or, according to the names of the first element in each subgroup***

1. Li and Be (H and He);
2. B, C, N, O, F, and Ne;
3. Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, and Zn;
4. La, Ce, Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tu, and Yb.

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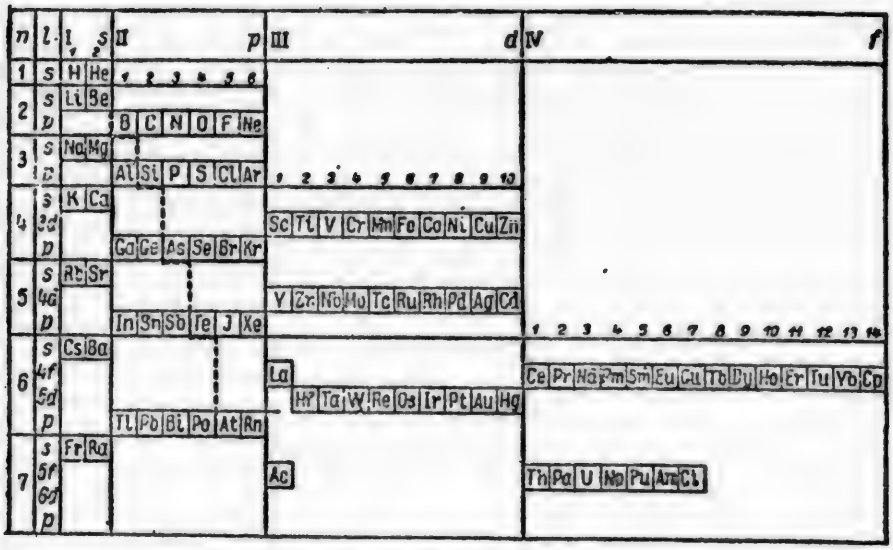
* More correctly, according to the designation of the last state to be filled. The electronic formula: the coefficient is the principal quantum number; the letter is the subsidiary quantum number; the exponent is the number of electrons; for curium, for example:

$1s^2 2s^2 2p^6 3s^2$, $3p^6 4s^2 3d^{10} 4p^6 5s^2 4d^{10} 5p^6 6s^2 4f^{14} 5d^{10} 6p^6 7s^2 5f^7 6d$.

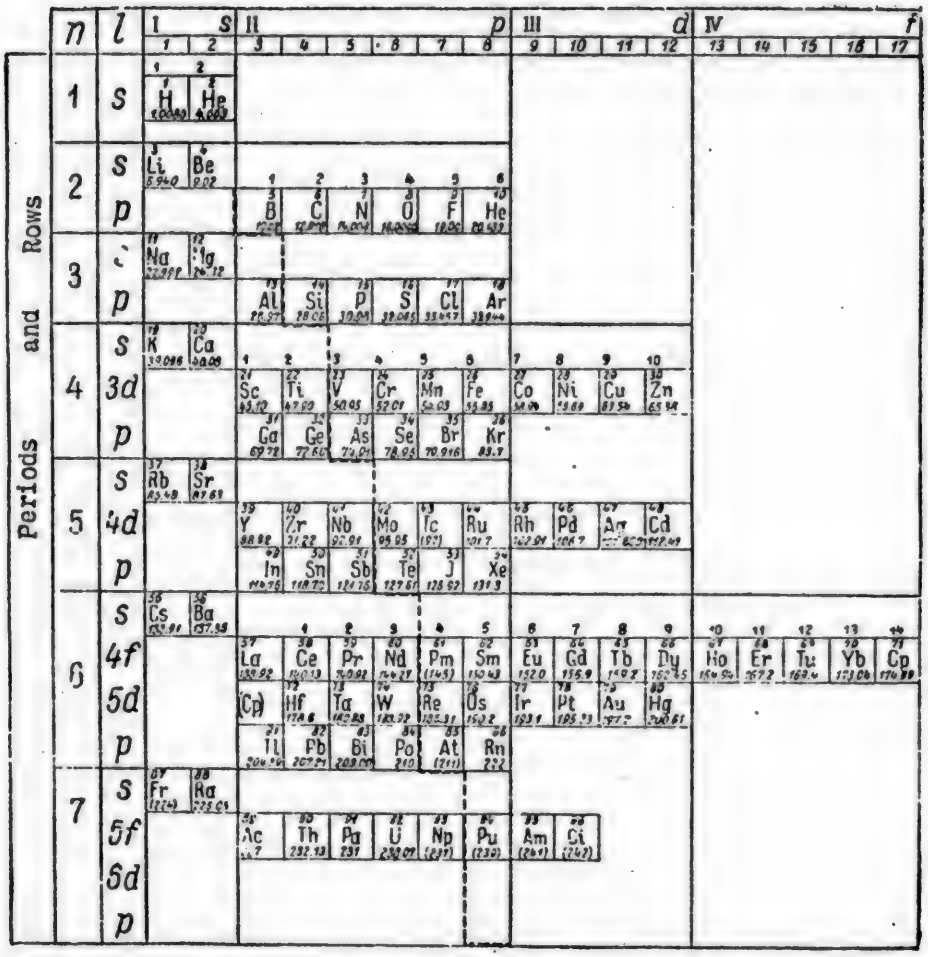
** The repeatability of the configuration of the outer electron shells, strictly speaking, also determines the periodicity of the chemical properties of the elements.

***The elements in the subgroups are displaced along the verticals analogously to the displacement of the main group and subgroup in the classic table. Of interest is the "fortuitous" falling of the unstable elements (technetium, prometheum, astatine, neptunium, but not francium) in a single column of the table. [Cf Uspekhi Khimii (Progress in Chemistry), 16, 614 (1947) for the nomenclature of the artificial elements].


n
l
s
II p
III d
IV f
1 s H He
2 s Li Be
2 p B C N O F Ne
3 s Na Mg
3 p Al Si P S Cl Ar
4 s K Ca
4 3d Sc Ti V Cr Mn Fe Co Ni Cu Zn
4 p Ga Ge As Se Br Kr
5 s Rb Sr
5 4d Y Zr Nb Mo Tc Ru Rh Pd Ag Cd
5 p In Sn Sb Te J Xe
6 s Cs Ba
6 4f La Ce Pr Nd Pm Sm Eu Gd Tb Dy Ho Er Tu Yb Cp
6 5d Hf Ta W Re Os Ir Pt Au Hg
6 p Tl Pb Bi Po At Rn
7 s Fr Ra
7 5f Ac Th Pa U Np Pu Am Cl

"Long" Table

Groups and Subgroups


Periods and Rows
n
l
I s
II p
III d
IV f
1 s H He
2 s Li Be
2 p B C N O F He
3 s Na Mg
3 p Al Si P S Cl Ar
4 s K Ca
4 3d Sc Ti V Cr Mn Fe Co Ni Cu Zn
4 p Ga Ge As Se Br Kr
5 s Rb Sr
5 4d Y Zr Nb Mo Tc Ru Rh Pd Ag Cd
5 p In Sn Sb Te J Xe
6 s Cs Ba
6 4f La Ce Pr Nd Pm Sm Eu Gd Tb Dy Ho Er Tu Yb Cp
6 5d (Cp) Hf Ta W Re Os Ir Pt Au Hg
6 p Tl Pb Bi Po At Rn
7 s Fr Ra
7 5f Ac Th Pa U Np Pu Am Cl

"Short" Table

Thus:

The s-group has 2 subgroups;
The p-group has 6 subgroups;
The d-group has 10 subgroups;
The f-group has 14 subgroups (7 subgroups of which are incomplete).

Each element in the table is denoted by a symbol and two generally accepted constants — its atomic number and its atomic weight, the element's place in the table being determined by two co-ordinates: its row and its subgroup.

It should be borne in mind that this proposed form of the table, which retains the existing division of the elements into groups and subgroups in the classical sense, allocates them differently within the system; it is noted that the "horizontal similarities" predominate over the "vertical" and the center of gravity is shifted from the subgroup to the row, from valency to the electron state.

Elements with identical numbers and states of the electrons in the outer shell and lying in identical subgroups in rows of periods of equal length: the 2nd and the 3rd, the 4th and the 5th, the 6th and the 7th, one beneath the other, such as: Li – Na, Ba – Ra, B – Al, Sc – Y, and Gd – Ci, are the closest analogues of each other. This facilitates the explanation of the so-called secondary periodicity.

The traditional division of the elements into metals and nonmetals becomes more precise.

1. s-, d-, and f- elements are all metals; moreover:

$s^1$-elements are alkali metals;
$s^2$-elements are alkaline earths;
d-elements are complex-constituents;
4f-elements are the lanthanoids;
5f-elements are the actinoids.

2. p-elements are divided into metals and nonmetals by the following diagonal boundary (from top left to bottom right):

Be – B, Al – Si, Ge – As, Sb – Te, Po – At,

the $p^5$-elements being halogens.
the $p^6$-elements being inert gases.

Rejecting use of the valency principle in the construction of the table made it possible to:

1) Maintain the closest possible approximation to the classic table of Mendeleyev in its "short" variant;

2) Eliminate the artificialty of placing of the elements in Group VIII and, to some degree, of those in the 1st and 2nd subgroups;

3) Fit the lanthanoids into the system;

4) Keep the length of the periods; and

5) Graphically express the physical essence of the periodic law and the electron structure of the elements' atoms.

This sort of construction for the table is all the more justifiable as valency is determined by the state of the atom and the number of loose electrons to be used; these may run as high as nine. Thus, the old, classical, form of the table, in which a whole generation of chemists was trained and to which science is indebted for many discoveries and researches, simply and strikingly discloses its quantum-mechanical content.

The difficulties in constructing the table are as follows:

a) The lack of a classification of the elements according to the structure of the atom nuclei;

b) The impossibility of classifying the elements according to values of the magnetic (m) and the spin (s) quantum numbers within the confines of each period;

c) The presence of "anomalies" in filling the electron levels of some d- and f-elements, which are determined by the stability of the fully and half-filled shells:

1. Cr, 2. Cu, 3. Nb – Ag, 4. La – Yb, 5. Ir – Au, 6. Ac — Ci;

d) The special position of hydrogen and helium in the system, which is justified by the electron structure of their atoms and the absence of close analogues.*

Relying on the periodic law and possessing experimental data**, we may assert that the lanthanoid series obviously begins with La and ends with Yb, since Ce exhibits, not the first f-electron, but suddenly two of them, whereas Yb has a complete f-shell. It is probable that the same can be said of the actinoid series on the basis of their analogy with the lanthanoids.

In conclusion, the author expresses his thanks to Prof. S. A. Shchukarev for his valuable suggestions.

## CONCLUSIONS

The quantum-mechanical form of the periodic system is set forth on the basis of a classification of the elements according to their quantum numbers.

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* It is not impossible that this is due to the special role of protons (p) and helions [alpha particles] ($\alpha$) in the structure of atomic nuclei and nuclear reactions.

** C.f. W. Meggers, Science, 105, 514 (1947) for example.

# THERMAL ANALYSIS OF THE DIOXANE - PHOSPHOROUS ACID SYSTEM

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In one of my papers[1] I described the results of the thermal analysis of the dioxane-pyrosulfuric acid system. In the melting point - composition diagram for this system, two eutectics and one dystectic were found, the latter corresponding to the dioxanate of pyrosulfuric acid, the composition of which is expressed by the following formula:

$$H_2S_2O_7(C_4H_8O_2)_2.$$

The present paper describes the results of the thermal analysis of the dioxane-phosphorous acid system.

The research method was the same as in the previous paper [1].

The dioxane was prepared as before [1], its melting point coinciding with that given by Hess and Frahm [2].

The phosphorous acid was supplied by Kahlbaum; its m.p. was 72.31°.

## EXPERIMENTAL RESULTS

Four series of test runs were made to determine the cooling curves, starting with pure dioxane and ending with phosphorous acid, and, conversely, starting with pure phosphorous acid and ending with dioxane. In the four series, 36 temperature-time curves were taken in all. These curves were used to determine the first temperature standstill as crystals are formed in the solution.

The cooling mixture used was either water-ice or ice-water-calcium chloride. In the event of extremely pronounced supercooling of the systems and the absence of any crystallization from the solution, resort was had to cooling with "dry ice".

All the results are listed in the general table below and in the graph illustrating the tabular data.

As may be seen from the table, the first series of points was obtained by increasing the percentage of the phosphorous acid to a high of 15.8%. When we follow the change in temperature of the crystallization of $H_3PO_3$ solutions in dioxane in this section of the curve, we notice how extremely slowly it drops. For example, if pure dioxane crystallizes at +11.78°, the solution of Point 7, containing only 84% of dioxane, crystallizes at +9.19°.

The second series of points was obtained by repeating the test in the same sequence, i.e., from pure dioxane, in order to check the results in two independent runs.

The third series begins with pure phosphorous acid (Point 24) and continues with rising percentages of dioxane in phosphorous acid, breaking off at Point 8, where the (mol.) percentage of dioxane has reached 83.25%. At minus temperatures, the cooling mixture used was a mixture of ice-water-salt.

As we see from the same table, the points from 17 to 20, which cover the range from 26.41% to 43.53% of dioxane, were not measured in this run, owing to pronounced supercooling.

In order to obtain results in this region, a fourth test run IV was made with solid carbon dioxide used as the refrigerant. As is seen from the data of this run, the supercooling of the system went as low as $-20^{\circ}$ and $-37^{\circ}$. The liquid system became very viscous, hardly mobile at all. Crystallization could be produced, however, by stirring.

THERMAL ANALYSIS OF THE DIOXANE-PHOSPHOROUS ACID SYSTEM

| Run | Point | Mol.% of dioxane in the system | Crystallization temperature | Remarks |
|---|---|---|---|---|
| I | 1 | 100.00 | 11.78 | |
| | 2 | 98.8 | 11.32 | |
| | 3 | 92.5 | 10.36 | |
| | 4 | 90.8 | 10.11 | |
| | 5 | 89.0 | 9.79 | |
| | 6 | 86.1 | 9.35 | |
| | 7 | 84.2 | 9.19 | |
| III | 8 | 83.25 | 8.31 | |
| | 9 | 75.03 | 7.92 | |
| | 10 | 74.20 | 7.34 | |
| | 11 | 69.99 | 6.8 | |
| | 12 | 63.75 | 6.0 | |
| | 13 | 63.50 | 4.0 | |
| | 14 | 63.50 | -1.5 | |
| | 15 | 55.58 | -2 | |
| | 16 | 53.79 | -5 | |
| | 17 | 43.53 | Cooling down to $-12.5^{\circ}$ produces no crystallization | Supercooled, colorless, transparent liquid, very viscous |
| | 18 | 40.01 | | |
| | 19 | 36.67 | | |
| | 20 | 26.41 | The same | |
| | 21 | 20.79 | +41.0 | |
| | 22 | 16.42 | 49 | |
| | 23 | 12.56 | 56.1 | |
| | 24 | 0.00 | 72.31 | |
| II | 25 | 100.00 | 11.78 | |
| | 26 | 97.25 | 11.25 | |
| | 27 | 83.60 | 9.68 | |
| | 28 | 79.01 | 8.99 | |
| | 29 | 75.42 | 8.11 | |
| | 30 | 73.10 | 7.92 | |
| | 31 | 66.51 | 6.61 | |
| IV | 32 | 22.2 | +36.1 | Supercooled to $-37^{\circ}$ |
| | 33 | 29.98 | 22.5 | |
| | 34 | 39.9 | 3.7 | Supercooled to $-19^{\circ}$ |
| | 35 | 47.8 | 11.5 | to $-21^{\circ}$ |
| | 36 | 53.49 | - 4 | |

The temperatures recorded in the table for this series of points, however, refer to the melting points of the crystals produced in the supercooled liquid.

The melting point-composition curve plotted from these data provides the following picture (of graph).

The whole curve consists of two branches:

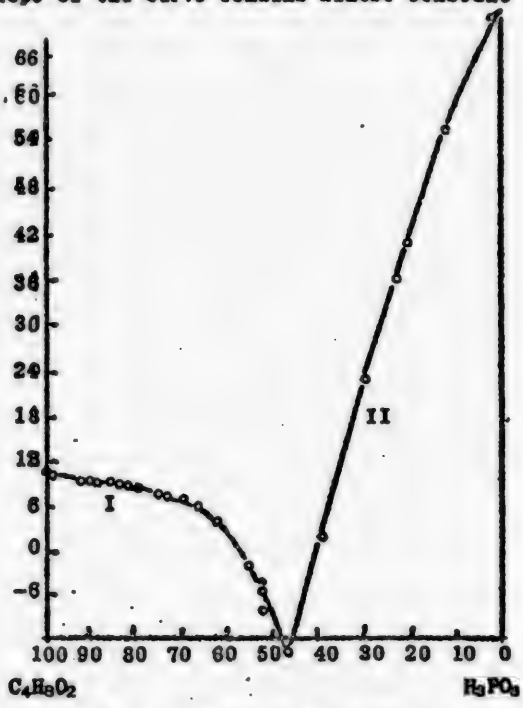
The first (I), for the solutions of phosphorous acid in dioxane, and the second (II), for the solutions of dioxane in phosphorous acid.

When we examine the curve, we notice that the temperature gradient of Curve I is sharply different from that of Curve II. The addition of small quantities of dioxane to phosphorous acid is accompanied by an extremely sharp drop in the temperature of crystalliza-

tion of the solution (Curve II); moreover, the slope of the curve remains almost constant down to the eutectic point.

As is seen in the graph, the composition-temperature diagram of this system has only one eutectic, located below zero temperature.

Curve I, for solutions of phosphorous acid in dioxane, is somewhat different. The freezing temperature of the solutions drops only slightly until 30 (mol) percent of phosphorous acid. This is all the more interesting in that the cryoscopic constant of dioxane is more than two and one-half times that of water, equalling 4.88° [2]. It must be assumed that in this region the solutions of phosphorous acid are strongly polymerized, with 3 to 4 molecules of $H_3PO_3$ in a single kinetic unit. Beginning at about 35% and down to the eutectic point, the temperature gradient increases sharply. From this diagram the conclusion must be drawn that there is no chemical affinity between dioxane and phosphorous acid.




Thermal Analysis of the Dioxane – Phosphorous Acid System

## CONCLUSIONS

1. The dioxane-phosphorous acid system was investigated by the method of thermal analysis.

2. A melting point-composition curve was plotted from the data of this analysis.

3. The fact that this diagram exhibits only one eutectic point indicates the absence of chemical action between dioxane and phosphorous acid.

Hence, no constant solution (crystallosolvate) of dioxane and phosphorous acid is formed under ordinary conditions.

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# DETERMINATION OF TRANSFERENCE NUMBERS IN SODIUM TETRABORATE GLASSES

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1. The accurate knowledge of the magnitude of transference numbers of ions is of great significance for the understanding of the structure of an electrolyte and the mechanism of its conductivity. Confirmation of the ionic character of the conductivity of glasses has been the object of numerous investigations. In 1884, Warburg [1], investigating sodium silicate glass, confirmed the ionic character of its conductivity. As anode, he utilized a sodium amalgam, while pure mercury served as cathode. During the passage of a continuous current, the mercury cathode was enriched with sodium, whose quantity corresponded to that theoretically calculated according to Faraday's law. The weight of the glass remained unchanged; thus the ionic character of conductivity in ordinary glass was demonstrated. Later, Le-Blanc and Kerschbaum [2] as well as other investigators confirmed the applicability of Faraday's law to glasses. The analogous character of the conductivity in simple sodium borate and phosphate glasses was disclosed by S. A. Shchukarev and P.P. Koboko [3]. In these glasses the investigators showed the existence of polarization, testifying to the movement of the sodium ions. However, an accurate determination of transference numbers in glasses, according to the method of Tubandt [4], so far as the author is aware, has not yet been made by any one.

2. As is known, the method developed by Tubandt was applied to crystallized materials. Three cylinders of a pressed powder of the material being investigated were tightly gripped between two electrodes and an electric current passed through them. In series with the cylinders was included a silver coulometer. It was found that an explanation of the character of the conductivity and calculation of the transference numbers was possible on the basis of the data on the change of weights of cathode and anode cylinders and the anode layer, under the condition of constancy of weight of the intermediate cylinder.

In the present investigation, the glass was prepared from $Na_2B_4O_7 \cdot 10H_2O$.

Borax was melted in a platinum crucible at a temperature of 800-1000°. After reaching a transparent, uniform consistency (absence of bubbles in the melt) the melt was poured upon a steatite plate in the form of large drops, which took on the shape of flat disks. The resultant glass was subjected to slow heating continuously for 7 to 8 hours. The initial temperature of heating was about 450°. It was lowered every hour by 50°. The resultant disks were ground and polished. Three such polished flat disks, 18 mm. in diameter and about 1 mm in thickness, were held between a silver disk, serving as anode, and a glass tube filled with mercury, which was the cathode. The electrodes together with the glass disks held between them were then transferred to an electric oven, whose temperature was maintained at 300°. The arrangement of the oven, as well as the basic method of insertion, were as described in the work of S. A. Shchukarev [5]. The temperature was determined by a thermocouple. Across the electrodes there was impressed a potential difference of about 300 V. In series with the glasses being investigated was included a silver coulometer. After 4 to 6 hours of passage of the current, the circuit was disconnected, and the oven temperature gradually lowered to

room temperature, in order to guard against cracking of the glass. As a result of the passage of silver into the anode glass, it had taken on a brown color.

The anode and middle glasses were weighed both before the experiment and after the passage of the current; the weight of silver deposited in the coulometer was also determined.

The cathode glass was not weighed. As a result of intimate contact with mercury it was seriously contaminated. A control determination of the deposit of sodium in the cathode mercury was likewise not carried out. The transference numbers were determined by ascertaining the change in weight of the anode glass along with the amount of silver deposited in the coulometer. As a control of the amount of silver which had entered the anode glass, a direct determination by titration was made. For this purpose, the anode glass was dissolved in a weak solution of nitric acid and titrated with potassium rhodanate, according to Volhard's method. These figures are given in column 13 of the table, designated by $g_2'$.

3. In order to understand the results obtained and to explain by their means the character of the conductivity of the glass, we shall here consider the possible types of conductivity of glasses.

a) Purely electronic electrical conductivity of glass. Obviously in this case the weight of the anode glass must remain unchanged on passage of the current. Change in weight of the anode glass $g_1^0 = 0$.

b) Transference of electricity in the glass takes place exclusively by means of cations. Thanks to substitution in the anode glass of sodium ions by silver ions, the anode glass must increase its weight by the quantity:

$$g_1^+ = g_2 \cdot \frac{107.88 - 23.00}{107.88},$$

where $g_2$ is the weight of silver that has passed into the glass, equal to the weight of silver deposited in the coulometer. 23.00 and 107.88 are the atomic weights of sodium and silver.

c). Conductivity takes place exclusively by means of anions, such as $O^=$. The anode glass must increase in weight by an amount equal to the weight of silver oxide (or other compound of silver with a corresponding anion) and equivalent to the quantity deposited in the silver coulometer:

$$g_1^- = g_2 \cdot \frac{107.88 + x}{107.88} = g_1^+ \left| 1 + \frac{23.00 + x}{107.88 - 23.00} \right|,$$

where x is the equivalent weight of the anion, and the other symbols have the same meaning as before.

d) The electrical conductivity of the glass depends on the mobility of the sodium cations as well as upon anions, such as the ionized atoms of oxygen. The anode glass must increase in weight as a result of the partial substitution of sodium by silver, as well as by the formation on the boundaries of the electrodes of the products of interaction of silver with discharged anions. In this case:

$$g_1^{\pm} = \eta_{Na} \cdot g_2 \cdot \frac{107.88 - 23}{107.88} + \eta_x \cdot g_2 \cdot \frac{107.88 + x}{107.88} =$$

$$= g_2 \cdot \frac{107.88 - \eta_{Na} \cdot 23 + \eta_x \cdot x}{107.88} = g_1^+ \left[ 1 + \frac{(23 + x)\eta_x}{107.88 - 23} \right],$$

where $\eta_{Na}$ and $\eta_x$ are transference numbers of cations and anions.

Thus, in case a), the weight of the anode glass must remain unchanged. The greatest change in weight of the anode glass can be expected in case c), the least in case b), and a quantity intermediate between them in case d), i.e.:

| No. of experiment | Conditions of experiment: Temp. (T) and Time (t). | Change in middle glass | Weight of anode glass disk | | Weight of middle glass disk | | Weight of coulometer | | Anode glass $S_1$ (experimental) | Coulometer $S_2$ | $g_1^+$ (Calculated) | $g_2^1$ (analytical) | $\frac{g_2^1}{S_2}$ | $\eta_{Na^+}$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | Before expt. | after expt. | Before expt. | After expt. | Before expt. | After expt. | | | | | | |
| 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 | 12 | 13 | 14 | 15 |
| 1 | T = 270° t = 2 hr.20m. | −0.0002 | 0.4927 | 0.4975 | 0.8266 | 0.8264 | 24.6408 | 24.6468 | 0.0048 | 0.0060 | 0.0017 | 0.0060 | 1.00 | 1.02 |
| 2 | T = 270° t = 6.5 hr. | 0.0000 | 0.5314 | 0.5398 | 0.5413 | 0.5413 | 24.6476 | 24.6582 | 0.0084 | 0.0106 | 0.0081 | 0.0106 | 1.00 | 1.01 |
| 3 | T = 320° t = 5 hr. | −0.0004 | 0.5257 | 0.5367 | 0.5402 | 0.5398 | 24.6419 | 24.6556 | 0.0110 | 0.0137 | 0.0106 | 0.0134 | 0.98 | 1.02 |
| 4 | T = 300° t = 6 hr. | 0.0000 | 0.7503 | 0.7681 | 0.4334 | 0.4334 | 24.6516 | 24.6744 | 0.0178 | 0.0228 | 0.0179 | 0.0218 | 0.96 | 1.00 |
| 5 | T = 300° t = 4 hr. | +0.0001 | 0.6363 | 0.6424 | 0.5870 | 0.5871 | 24.6564 | 24.6644 | 0.0061 | 0.0080 | 0.0063 | 0.0078 | 0.98 | 0.97 |
| 6 | T = 300° t = 5hr. | +0.0001 | 0.6100 | 0.6228 | 0.4962 | 0.4963 | 24.6614 | 24.6763 | 0.0128 | 0.0149 | 0.0118 | 0.0160 | 1.06 | 1.08 |
| 7 | T = 300° t = 4 hr. | +0.0001 | 0.4873 | 0.4931 | 0.6184 | 0.6185 | 24.5975 | 24.6065 | 0.0058 | 0.0070 | 0.0055 | 0.0075 | 1.07 | 1.05 |
| | | | | | | | | | | | | | 1.01 | $1.02 \pm 0.02$ |

$$g_2^{\sim} > g_2^{\pm} > g_1^{+} > g_1^{\theta} = 0.$$

The transference numbers of the sodium ions in the glass can be calculated according to the following formula:

$$\eta_{Na^+} = \eta_{Ag^+} = \frac{\frac{g_1}{107.88 - 23}}{g_2 / 107.88},$$

where $g_1$ is the change in weight of the anode glass (experimental);

$g_2$ is the weight of silver deposited in the coulometer.

In all, 9 experiments were conducted. In the table are given the results of only 7 experiments. The first two experiments, as a result of several faults in the set up of apparatus, which were later corrected, gave by far the worst results, and are not reported here. From columns 6, 7, and 3 of the table, it is clear that in conformity with the requirements of the method, the weight of the intermediate glass disk remained practically unchanged. The figures given in columns 4, 5 and 10 and also 8, 9, and 11, exclude the above indicated types of electronic conductivity. Actually, the anode glass increased in weight upon passage of the current, as can be seen from the figures of columns 11, 12, 13, and 14, strictly in conformity with Faraday's law. The latter demonstrates the purely ionic character of the conductivity of the glass.

The figures of columns 10 -- 12 and 15 exclude cases c) and d), as the experimental determination of the increase in weight of the glass corresponds to the calculated value according to the formula for case b) within the limits of experimental error. The result shows that only the sodium ion carries the current in the glass.

The experimental figures permit us to conclude that: 1) sodium tetraborate glass possesses ionic conductivity, which takes place according to Faraday's law with an accuracy up to 2%; 2) only the cations take part in carrying the current in the glass, in this particular case the sodium ions, the remaining ions being immobile.

## CONCLUSIONS

1. An investigation of transference numbers in borax glass has been carried out.

2. The purely ionic character of conductivity in alkaline borate glass has been confirmed.

3. It has been determined quantitatively that the conductivity of the glass is due exclusively to the sodium cations, whose transference number is $\eta_{Na^+ cp} = 1.02 \pm 0.02$. The remaining ions are immobile and take no part in the electrical conductivity.

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# INVESTIGATION OF THE MELTING POINTS OF THE QUADRUPLE SYSTEM OF THALLIUM, SILVER, POTASSIUM AND SODIUM NITRATES

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## Introduction

Up to the present time there has been no description in the literature of the melting points of a quaternary salt system with a common ion, although work in this direction has been and continues to be done. Thus, V.P. Radishchev has experimentally studied the two quaternary systems: NaF-NaCl-NaBr-NaI and KF-KCl-KBr-KI [1]. It is also known that the system 1) LiF-NaF-KF-$MgF_2$ has been studied by A.G. Bergman, E.P. Dergunov and I.N. Nikinova [2], and the system 2) NaCl-KCl-$CaCl_2$-$BaCl_2$ by A.G.Bergman and A.K.Klimentov. In the department of general and inorganic chemistry of the Voronezh State University (VGU) Y.A. Ugay has completed a study of the quaternary system NaCl-KCl-$CaCl_2$-$PbCl_2$.

A theoretical analysis has been given only for one of the simplest types of chemical diagrams of quaternary systems with a common ion, especially in the case where there is no chemical interaction of components or formation of solid solutions, and in the case of simple eutectic melting points [3].

Other types of chemical diagrams of quaternary systems have apparently even been ruled out of theoretical consideration, as a result of the nature and character of the tetrahedral face systems. In fact, having no examples of genuine chemical diagrams, it is natural to arrive at mistaken conclusions.

We have conducted a study of the quaternary system of thallium, silver, potassium, and sodium nitrates. In this system it is possible to note the similarity of the higher melting nitrates of potassium and sodium (melting points 337 and 308°respectively) and the lower melting nitrates of silver and thallium (melting points 208 and 206° respectively). The binary component systems form solid solutions: continuous ($KNO_3$ +$NaNO_3$), with peritectic ($AgNO_3$ + $NaNO_3$) and with discontinuity ($TlNO_3$ + $KNO_3$ and $TlNO_3$ + $NaNO_3$), and chemical compounds: the congruent melting low temperature compound $TlNO_3 \cdot AgNO_3$ (melting point 83°) and the incongruent melting compound $AgNO_3 \cdot KNO_3$, also a comparatively low temperature compound (temperature of decomposition 136°). All the components of the systems have polymorphous forms, which has introduced special characteristics into the chemical diagram of the system studied.

The quarternary system studied by us has undoubted interest, especially from the point of view of developing our knowledge of the topology of the chemical diagrams of quarternary systems.

## EXPERIMENTAL

### Method of Investigation

The study of the quaternary system $TlNO_3$-$AgNO_3$+$KNO_3$+$NaNO_3$ was conducted by a visual

thermal method described by the author in a previous publication [4].

To measure the temperature, a thermocouple was used, consisting of alloys of noble metals (one wire of the thermocouple consisted of an alloy of 60% gold, 30% palladium, and 10% platinum; the other of an alloy of 90% platinum and 10% rhodium). This permitted operation without protective glass caps at the hot point of contact. It significantly decreased the inertia of the thermocouple. In addition, the thermocouple used possessed high sensitivity, which was especially important in work with low temperatures.

The thermo-electromotive force of the thermocouple used was determined with the aid of a millivoltmeter having a scale up to 17 mV. As reference points in the graduation of the thermocouple, the melting points of the following chemically pure compounds were used: naphthalene, 80.1°; benzoic acid, 121.4°; silver nitrate, 208°; sodium nitrate, 308°; potassium dichromate 397.5°. The initial compounds were purified before using.

In forming the quaternary system $TlNO_3$-$AgNO_3$-$KNO_3$-$NaNO_3$, there entered, as independent parts, six binary systems: $TlNO_3$ – $AgNO_3$, $TlNO_3$ – $KNO_3$, $TlNO_3$ – $NaNO_3$, $AgNO_3$ – $KNO_3$, $AgNO_3$ – $NaNO_3$ and $KNO_3$ – $NaNO_3$, and four ternary systems: $TlNO_3$ – $KNO_3$ – $NaNO_3$; $AgNO_3$ – $KNO_3$ – $NaNO_3$, $TlNO_3$ – $AgNO_3$ – $KNO_3$ and $TlNO_3$ – $AgNO_3$ – $NaNO_3$.

All of the binary and two of the ternary systems were studied. Below we shall consider the data in the literature referring to these systems.

## Binary Systems

System $TlNO_3$ – $AgNO_3$. The system was studied by van Eyk [5] and represents a binary system with a congruent chemical compound $TlNO_3 \cdot AgNO_3$, with a melting point at 83°. The compound $TlNO_3$-$AgNO_3$, as is obvious from the diagram (Fig. 1), is very unclearly shown. Van Eyk succeeded in demonstrating its existence only by transforming it into the polymorphous form at 26°.

Both eutectics correspond to a temperature of 81°, and compositions of 47.5% and 53% $AgNO_3$ respectively.*

System $TlNO_3$ – $KNO_3$: This system was studied by van Eyk [5]. The system has a diagram with a single eutectic and a limited range of solid solutions. The eutectic corresponds to a temperature of 182° and 70% $TlNO_3$. There are interesting changes in the solid phase, as is obvious from the diagram.

System $TlNO_3$ – $NaNO_3$: This system was studied by van Eyk and is characterized by a diagram with a limited range of solutions and a eutectic at 162° and 20.5% $NaNO_3$.

The liquidus curve of this system has been constructed according to data taken from the reference book T.E. [7], and is given in Fig. 3.

System $AgNO_3$ – $KNO_3$: This system was studied by Usanow [8]. It forms a chemical compound $AgNO_3 \cdot KNO_3$, which melts incongruously. The eutectic point corresponds to a temperature of 131° and a content of 37.7% $KNO_3$, the transition point to a temperature of 136.3° and 46% $KNO_3$. The diagram of the system is given in Fig. 4.

System $AgNO_3$ – $NaNO_3$. This system was studied by Hissink [9]. The diagram of this system (Fig. 5) shows solid solutions with a peritectic at 20% $NaNO_3$, and a temperature of 217°.

System $KNO_3$ – $NaNO_3$. This system has been studied by many different investigators. Carveth [10] and Hissink [9] give a diagram with a limited range of solid solutions and a eutectic at 217°; it is interesting to observe that this incorrect diagram has been taken over into many text and reference books. Later work (1923) by Briscoe and Madgin [11],

*Both here and further on in the entire work, without exception, percentages are molecular.

showed that this system gives a continuous series of solid solutions with a minimum at 225.7° and 45% $NaNO_3$. Prof. A.G.Bergman and numerous coworkers have subjected this system to an especially large number of verifications. An especially careful check of the system was made in 1938 by F.I. Vasenin and A.G.Bergman [12]. They give the diagram (Fig. 6) with continuous solid solutions and a minimum at 223° and 50% $NaNO_3$. We have accepted these latest figures.

### Ternary Systems

System $TlNO_3$ – $KNO_3$ – $NaNO_3$. This system was studied by P.K.Leban [13]. The diagram of the system (Fig. 7) is characterized by two principal fields of crystallization: the field of crystallization of $TlNO_3$; and the field of crystallization of continuous solid solutions ($KNO_3$ + $NaNO_3$). However, under the influence of the low-melting component ($TlNO_3$) the solid solutions at 150° separate, and as a result the system possesses a ternary eutectic point at 138° and a composition of 25% $NaNO_3$, 24% $KNO_3$ and 51% $TlNO_3$.

System $AgNO_3$ – $KNO_3$ – $NaNO_3$. This system was studied by A.P.Palkin and M.G.Turusov [14]. Its diagram (Fig. 7) has four principal fields of crystallization: 1) the field of crystallization of $AgNO_3$; 2) the field of $KNO_3$; 3) the field of $NaNO_3$; and 4) a small field of crystallization of the incongruent chemical compound $AgNO_3 \cdot KNO_3$. We may observe that in the given system, the continuous solid solutions ($KNO_3$ + $NaNO_3$) separate at 202°. As a result of the separation of the solid solutions in the system, there is a ternary eutectic at 116° and a composition of 42% $KNO_3$, 7% $NaNO_3$, 51% $AgNO_3$. The intersection of the eutectic and peritectic lines forms a ternary transition point at a temperature of 186° and a composition of 45% $KNO_3$, 20.7% $NaNO_3$, 34.3% $AgNO_3$.

System $TlNO_3$ – $AgNO_3$ – $KNO_3$. This system was studied by the author. The diagram of the system (Fig. 7) has five fields of crystallization. The binary compounds $TlNO_3 \cdot AgNO_3$ and $AgNO_3 \cdot KNO_3$, weakly expressed in binary regions, are here significantly developed; especially significant is the field of crystallization of the incongruous compound $AgNO_3 \cdot KNO_3$. In the region of the incongruous compound, the melt possesses great viscosity prior to crystallization. In the given system we have a ternary eutectic point at a temperature of 79° and composition 46.8% $TlNO_3$, 52.7% $AgNO_3$ and 0.5% $KNO_3$, and two ternary transition points: one in at 90° and 37.2% $TlNO_3$, 41% $AgNO_3$, and 21.8% $KNO_3$; the other at 80.5° and 45% $TlNO_3$, 33.5% $AgNO_3$, and 21.5% $KNO_3$.

System $TlNO_3$ – $AgNO_3$ – $NaNO_3$. This system was studied by the author. The diagram of the system (Fig. 7) shows four fields of crystallization. The projection of the space diagram (triangular isotherm) is characterized by a symmetrical field of crystallization. The fields of $TlNO_3$ and $AgNO_3$ have almost equal areas, a fact which is explained by the closeness of the melting points of these salts (206° and 208°)*.

There are two ternary eutectic points in the system, one corresponding to a temperature of 78° and a composition of 46% $TlNO_3$, 51.8% $AgNO_3$, and 2.2% $NaNO_3$; the other to a temperature of 79° and a composition of 51.3% $TlNO_3$, 46.4% $AgNO_3$, and 2.3% $NaNO_3$.

The diagrams of all the above described ternary systems are represented on Fig. 7, in which is shown the unfolded surface of the tetrahedron of our quaternary system.

### Quaternary System

System $TlNO_3$ – $AgNO_3$ – $KNO_3$ – $NaNO_3$. In the quaternary system under consideration $TlNO_3$ – $AgNO_3$ – $KNO_3$ – $NaNO_3$ (often called a salt system and written with regard to the ions, in this case Tl, Ag, K, Na $NO_3$) there are, as already mentioned above, 6 binary systems (edges of the tetrahedron) and 4 ternary systems (faces of the tetrahedron), reviewed above. All

* A statement on the influence of the melting points of the components on the character of the chemical diagram is found in the latest works of Prof. A.P.Palkin: "The development of the chemical diagram of mutually reacting ternary systems in melts", and "Characteristics of the composition diagrams of quaternary systems in melts".

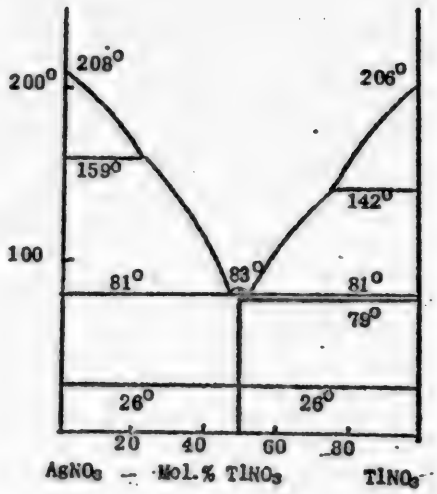


Fig. 1

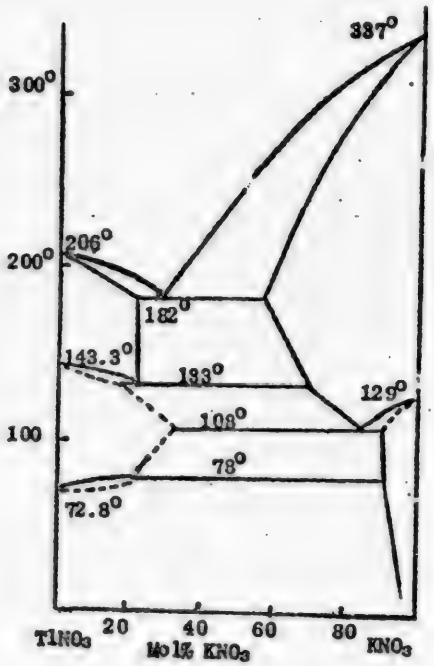


Fig. 2

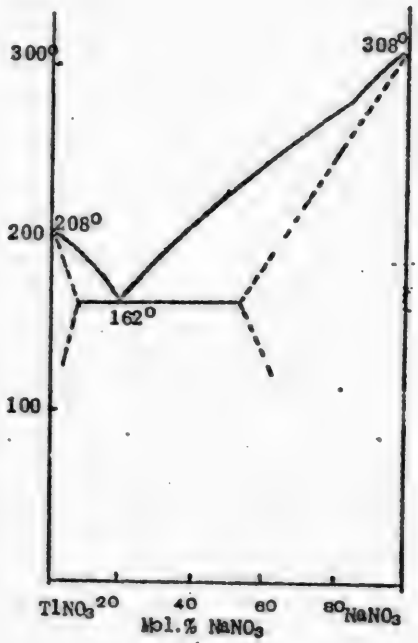


Fig. 3

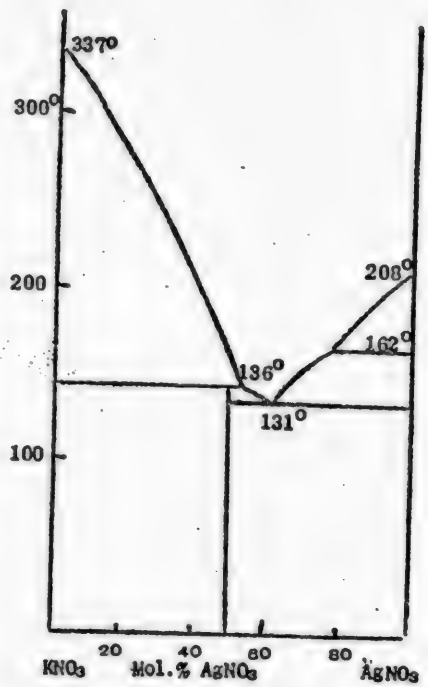


Fig. 4

the systems enumerated above together form the surface of the tetrahedron, whose unfolded form is shown in Fig. 7.

Just as the study of ternary systems can be conducted by the method of so called ternary cuts, which may be regarded as, and for the most part represented as, binary systems, so the study of quaternary systems can utilize the method of quaternary or internal sections. Every such section may be regarded and represented as (a complicated) ternary system. The study of quaternary sections is conducted in the same way as that of ternary systems, by the method of cuts, called in this case quaternary cuts, which are represented as binary systems.

We investigated the following 6 quaternary sections:

I (90% $AgNO_3$ + 10% $TlNO_3$) – $KNO_3$ – $NaNO_3$,
II (70% $AgNO_3$ + 30% $TlNO_3$) – $KNO_3$ – $NaNO_3$,
III (56% $AgNO_3$ + 44% $TlNO_3$) – $KNO_3$ – $NaNO_3$,
IV (50% $AgNO_3$ + 50% $TlNO_3$) – $KNO_3$ – $NaNO_3$,
V (35% $AgNO_3$ + 65% $TlNO_3$) – $KNO_3$ – $NaNO_3$,
VI (20% $AgNO_3$ + 80% $TlNO_3$) – $KNO_3$ – $NaNO_3$

The distribution of the sections is shown in Fig. 8.

TABLE 1

CUT I

90% (90% $AgNO_3$ + 10% $TlNO_3$) + 10% $NaNO_3$ ⟶ $KNO_3$

| No. of expt. | Mol.% $KNO_3$ | Temperature of beginning of crystallization |
|---|---|---|
| 1 | 0 | 194° |
| 2 | 8.32 | 179.9 |
| 3 | 18.29 | 159 |
| 4 | 22.03 | 150 |
| 5 | 28.99 | 135 |
| 6 | 33.29 | 125 |
| 7 | 35.25 | 119 |
| 8 | 37.45 | 123 |
| 9 | 39.54 | 125 |
| 10 | 42.21 | 131.5 |
| 11 | 45.09 | 147 |
| 12 | 50.06 | 167 |
| 13 | 58.59 | 201 |
| 14 | 65.09 | 222.5 |
| 15 | 74.38 | 257 |
| 16 | 85.97 | 292 |
| 17 | 92.63 | 310 |
| 18 | 96.44 | 323 |

TABLE 2

CUT II

75% (90% $AgNO_3$ + 10% $TlNO_3$) + 25% $NaNO_3$ ⟶ $KNO_3$

| No. of expt. | Mol. % $KNO_3$ | Temperature of beginning of crystallization |
|---|---|---|
| 1 | 0 | 221° |
| 2 | 12.71 | 197.5 |
| 3 | 23.14 | 176.6 |
| 4 | 35.07 | 151 |
| 5 | 40.74 | 136 |
| 6 | 45.31 | 155 |
| 7 | 50.55 | 180 |
| 8 | 59.48 | 214 |
| 9 | 67.65 | 241.5 |
| 10 | 78.83 | 278 |
| 11 | 84.32 | 296 |
| 12 | 89.02 | 306.4 |
| 13 | 95.47 | 322 |

## Quaternary Sections

Section I (90% $AgNO_3$ + 10% $TlNO_3$) – $KNO_3$ – $NaNO_3$. In the study of the given section, the following five quaternary cuts were made:

I [90% (90% $AgNO_3$ + 10% $TlNO_3$) + 10% $NaNO_3$] ⟶ $KNO_3$.
II [75% (90% $AgNO_3$ + 10% $TlNO_3$) + 25% $NaNO_3$] ⟶ $KNO_3$.
III [30% (90% $AgNO_3$ + 10% $TlNO_3$) + 70% $NaNO_3$] ⟶ $KNO_3$.
IV [73% (90% $AgNO_3$ + 10% $TlNO_3$) + 27% $KNO_3$] ⟶ $NaNO_3$.
V [62% (90% $AgNO_3$ + 10% $TlNO_3$) + 38% $KNO_3$] ⟶ $NaNO_3$.

Experimental results of the cuts are given in Tables 1, 2, 3, 4, 5, respectively.

Diagrams of the cuts are shown in Fig. 9.

The results of all the investigations on the first section are summarized in a diagram which is represented in Fig. 10 as a triangular isotherm.

TABLE 3

Cut III

30%(90% $AgNO_3$ + 10% $TlNO_3$), 70% $NaNO_3$ → $KNO_3$

| No. of expt. | Mol. % $KNO_3$ | Temperature of beginning of crystallization |
|---|---|---|
| 1 | 0 | 284° |
| 2 | 7.63 | 265 |
| 3 | 16.97 | 264.5 |
| 4 | 27.21 | 225 |
| 5 | 36.58 | 209.5 |
| 6 | 45.01 | 197 |
| 7 | 51.82 | 203 |
| 8 | 56.73 | 214 |
| 9 | 62.12 | 226 |
| 10 | 68.79 | 243 |
| 11 | 77.03 | 264 |
| 12 | 84.15 | 287 |
| 13 | 90.98 | 306 |
| 14 | 95.61 | 321 |

TABLE 4

Cut IV

73%(90% $AgNO_3$ + 10% $TlNO_3$), 27% $KNO_3$ → $NaNO_3$

| No. of expt. | Mol. % $NaNO_3$ | Temperature of beginning of crystallization |
|---|---|---|
| 1 | 0 | 138° |
| 2 | 2.25 | 139 |
| 3 | 5.28 | 142 |
| 4 | 9.10 | 147 |
| 5 | 12.43 | 152 |
| 6 | 14.58 | 157 |
| 7 | 17.77 | 167 |
| 8 | 21.21 | 183 |
| 9 | 25.69 | 196 |
| 10 | 30.23 | 206 |
| 11 | 39.87 | 222 |
| 12 | 49.78 | 238 |
| 13 | 59.44 | 253 |
| 14 | 71.63 | 268.4 |
| 15 | 82.02 | 283 |
| 16 | 86.91 | 289 |
| 17 | 92.79 | 298.5 |

TABLE 5

Cut V

62%(90% $AgNO_3$ + $TlNO_3$), 38% $KNO_3$ → $NaNO_3$

| No. of expt. | Mol.% $NaNO_3$ | Temp. of beginning of crystallization |
|---|---|---|
| 1 | 0 | 127° |
| 2 | 1.37 | 125.4 |
| 3 | 3.24 | 123 |
| 4 | 5.78 | 119 |
| 5 | 9.35 | 124.4 |
| 6 | 12.87 | 139 |
| 7 | 16.91 | 156 |
| 8 | 22.31 | 174 |
| 9 | 29.90 | 196 |
| 10 | 38.34 | 214 |
| 11 | 48.88 | 230 |
| 12 | 59.12 | 248.5 |
| 13 | 72.29 | 268 |
| 14 | 84.95 | 286 |
| 15 | 92.37 | 299 |

With regard to general appearance and character, the diagram of the first section (as was to be expected from its location) is strongly reminiscent of the diagram of the tetrahedral face system:

$$AgNO_3 - KNO_3 - NaNO_3$$

A few differences are the slight increase in size and the change in form of the field of crystallization of the compound $AgNO_3 \cdot KNO_3$, and a small increase in the field of the continuous solid solutions ($KNO_3$ + $NaNO_3$) in the vicinity of the compounds $KNO_3$ and $NaNO_3$.

The separation of the solid solutions is observed at a temperature of about 200°. In the respective fields of crystallization there are shown the lines of polymorphous transformation of $AgNO_3$ (159°), $KNO_3$ (129°) and the transformation of the second variety of $KNO_3$ (315°) and $NaNO_3$ (275°). The diagram possesses two ternary transition points: one, formed by intersecting eutectic and peritectic lines, has a temperature of 143° and the composition 4.1% $TlNO_3$, 86.9% $AgNO_3$, 4.3% $KNO_3$ and 1% $NaNO_3$; the other, 114° and the composition 5% $TlNO_3$, 45% $AgNO_3$, 40% $KNO_3$ and 10% $NaNO_3$.

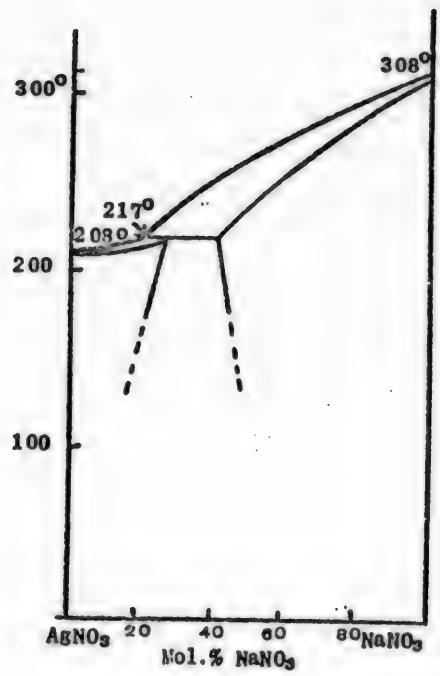


Fig. 5

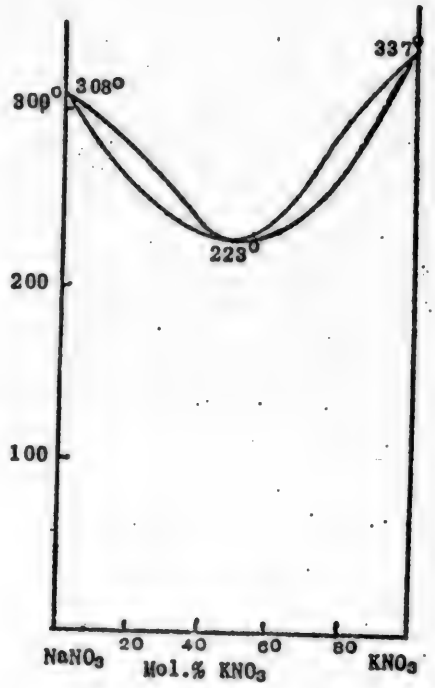


Fig. 6

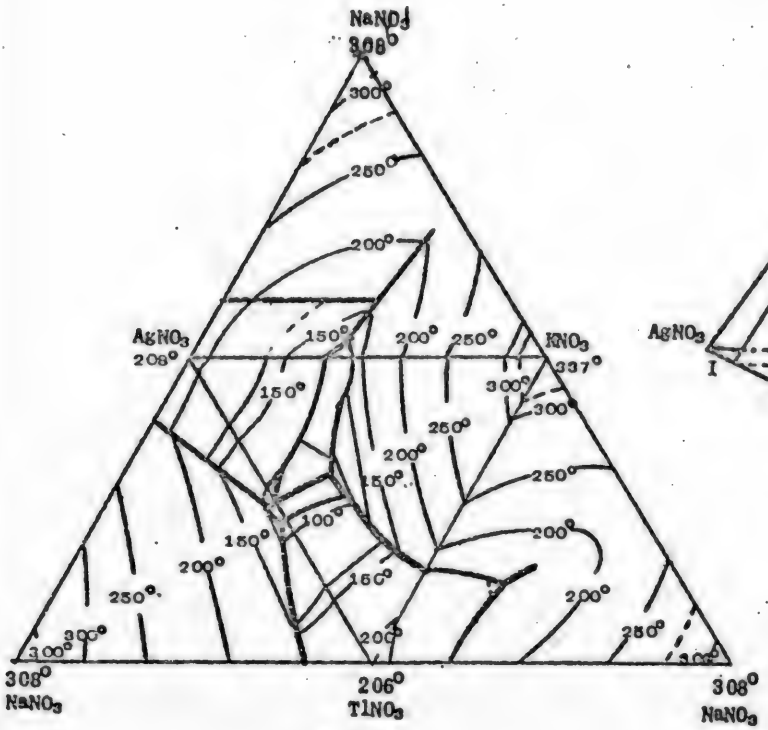


Fig. 7

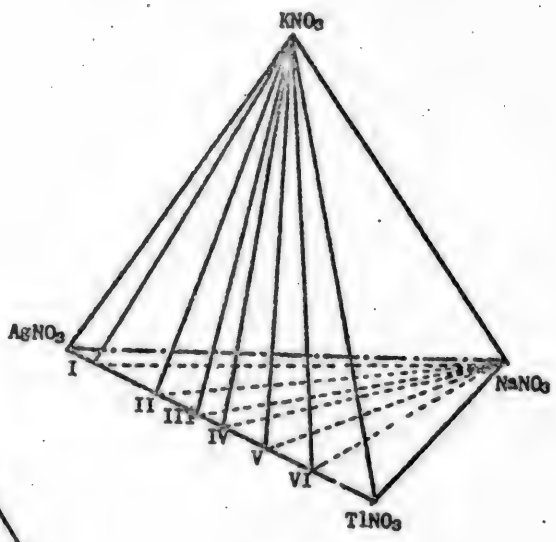


Fig. 8

Section II (70% $AgNO_3$ + 30% $TlNO_3$) – $KNO_3$ – $NaNO_3$. For the study of the given section, there were investigated: the pseudo binary system (70% $AgNO_3$ + 30% $TlNO_3$) – $NaNO_3$ and the 7 following quaternary cuts:

I [95% (70% $AgNO_3$ + 30% $TlNO_3$) + 5% $NaNO_3$] ⟶ $KNO_3$,
II [85% (70% $AgNO_3$ + 30% $TlNO_3$) + 15% $NaNO_3$] ⟶ $KNO_3$.
III [70.5% (70% $AgNO_3$ + 30% $TlNO_3$) + 29.5% $NaNO_3$] ⟶ $KNO_3$.
IV [40% (70% $AgNO_3$ + 30% $TlNO_3$) + 60% $NaNO_3$] ⟶ $KNO_3$,
V [80% (70% $AgNO_3$ + 30% $TlNO_3$) + 20% $KNO_3$] ⟶ $NaNO_3$.
VI [73% (70% $AgNO_3$ + 30% $TlNO_3$) + 27% $KNO_3$] ⟶ $NaNO_3$,
VIII [20% (70% $AgNO_3$ + 30% $TlNO_3$) + 80% $KNO_3$] ⟶ $NaNO_3$.

Experimental results are given in Tables 6, 7, 8, 9, 10, 11, 12, 13.

The diagrams of the pseudo binary system (70% $AgNO_3$ + 30% $TlNO_3$) — $NaNO_3$ and of the quaternary cuts are shown in Figs. 11 and 12.

The experimental results of Section II are summarized in a diagram shown in Fig. 13 as a triangular isotherm. The appearance and character of the given diagram resemble those of Section I, and are reminiscent of the diagram of the tetrahedral face system $AgNO_3$ – $KNO_3$ – $NaNO_3$. The differences noted in the description of the first cut are here expressed still

TABLE 6

70% $AgNO_3$, 30% $TlNO_3$ ⟶ $NaNO_3$

| Expt. No. | Mol % $NaNO_3$ | Temp. of beginning of crystallization |
|---|---|---|
| 1 | 0 | 140° |
| 2 | 1.89 | 141 |
| 3 | 4.62 | 143 |
| 4 | 7.74 | 144.5 |
| 5 | 9.78 | 150 |
| 6 | 11.05 | 159 |
| 7 | 14.37 | 172 |
| 8 | 18.90 | 187 |
| 9 | 26.41 | 207 |
| 10 | 35.08 | 228 |
| 11 | 46.95 | 250 |
| 12 | 59.18 | 265 |
| 13 | 71.83 | 277 |
| 14 | 83.00 | 290 |

TABLE 7 (Cut I)

95%(70% $AgNO_3$+30% $TlNO_3$), 5% $NaNO_3$ ⟶ $KNO_3$

| Expt. No. | Mol. % $KNO_3$ | Temp. of beginning of cryst. |
|---|---|---|
| 1 | 0 | 145° |
| 2 | 7.44 | 133 |
| 3 | 13.37 | 122 |
| 4 | 20.41 | 112 |
| 5 | 26.14 | 111 |
| 6 | 29.82 | 114 |
| 7 | 32.03 | 115 |
| 8 | 35.26 | 125 |
| 9 | 42.33 | 158 |
| 10 | 47.92 | 177 |
| 11 | 54.16 | 205 |
| 12 | 63.07 | 236 |
| 13 | 75.01 | 270 |
| 14 | 84.36 | 296 |
| 15 | 90.12 | 310 |
| 16 | 95.27 | 323 |

TABLE 8 (Cut II)

85%(70% $AgNO_3$+30% $TlNO_3$), 15% $NaNO_3$ ⟶ $KNO_3$

| Expt. No. | Mol % $KNO_3$ | Temp. of beginning of crystallization |
|---|---|---|
| 1 | 0 | 173° |
| 2 | 4.27 | 167 |
| 3 | 6.84 | 162 |
| 4 | 11.98 | 151 |
| 5 | 14.49 | 146 |
| 6 | 16.94 | 143 |
| 7 | 20.34 | 136 |
| 8 | 24.39 | 129 |
| 9 | 29.78 | 115 |
| 10 | 33.65 | 118 |
| 11 | 35.53 | 127.5 |
| 12 | 40.36 | 148.8 |
| 13 | 44.79 | 167 |
| 14 | 51.12 | 189 |
| 15 | 60.2 | 214 |
| 16 | 68.47 | 243 |
| 17 | 77.34 | 270 |
| 18 | 86.15 | 296 |
| 19 | 92.04 | 311 |
| 20 | 96.22 | 324 |

TABLE 9 (Cut III)

70.5%(70% $AgNO_3$+30% $TlNO_3$), 29.5% $NaNO_3$ ⟶ $KNO_3$

| Expt. No. | Mol % $KNO_3$ | Temp. of beginning of crystallization |
|---|---|---|
| 1 | 0 | 215° |
| 2 | 11.06 | 197 |
| 3 | 22.49 | 174.5 |
| 4 | 33.23 | 149.5 |
| 5 | 38.96 | 149 |
| 6 | 44.07 | 165 |
| 7 | 53.73 | 199 |
| 8 | 62.39 | 226 |
| 9 | 72.18 | 256 |
| 10 | 79.02 | 278 |
| 11 | 88.98 | 305 |
| 12 | 94.67 | 322.5 |

TABLE 10 (Cut IV)

40% (70% $AgNO_3$ + 30% $TlNO_3$), 60% $NaNO_3$ ⟶ $KNO_3$

| Expt. No. | Mol % $KNO_3$ | Temp. of beginning of crystallization | Expt. No | Mol% $KNO_3$ | Temp. beginning of crystalz. |
|---|---|---|---|---|---|
| 1 | 0 | 265° | 8 | 50.86 | 196° |
| 2 | 15.84 | 230 | 9 | 58.53 | 213 |
| 3 | 24.47 | 218 | 10 | 65.30 | 235 |
| 4 | 29.75 | 203 | 11 | 72.13 | 256 |
| 5 | 37.04 | 193 | 12 | 81.82 | 283 |
| 6 | 41.57 | 188 | 13 | 89.95 | 307 |
| 7 | 47.69 | 189 | 14 | 95.62 | 323.5 |

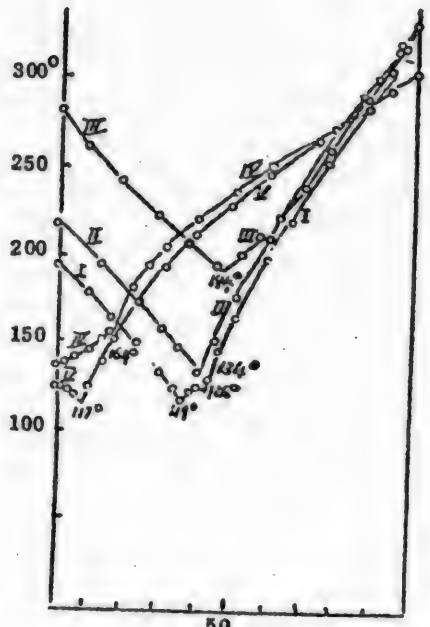


Fig. 9.

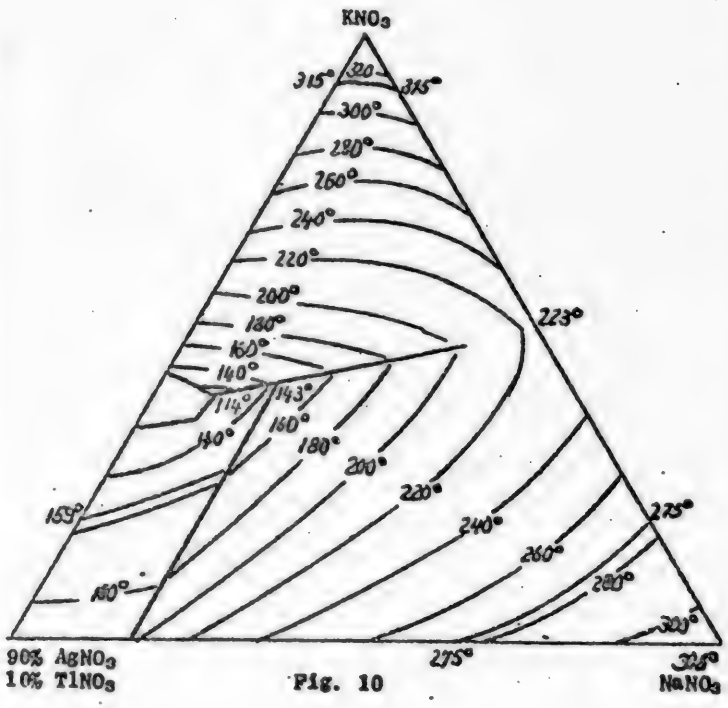


Fig. 10

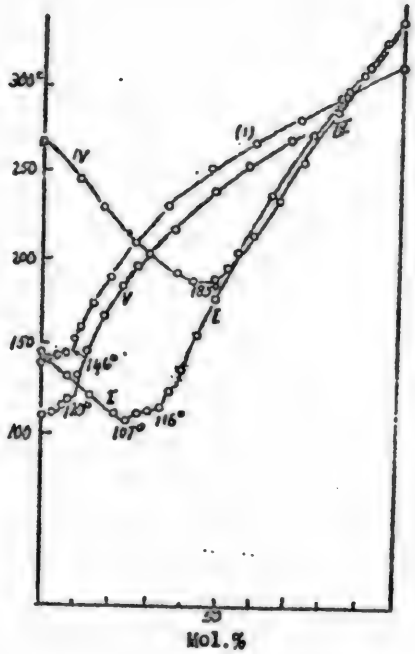


Fig. 11

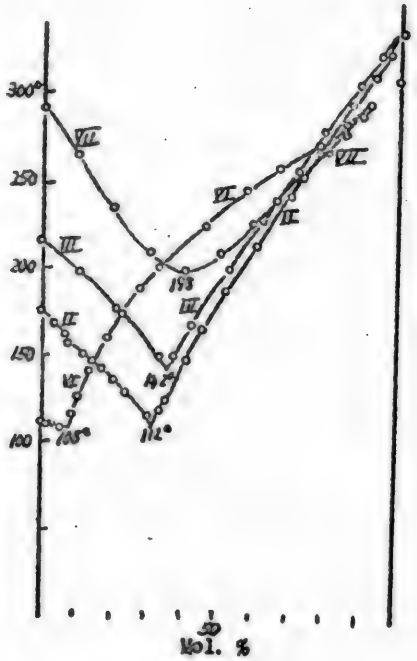


Fig. 12

TABLE 11 (Cut V)

80% (70% $AgNO_3$ + 30% $TlNO_3$) + 20% $KNO_3$ → $NaNO_3$

| Expt. No. | Mol.% $NaNO_3$ | Temp. of beginning of crystallization |
|---|---|---|
| 1 | 0 | 108° |
| 2 | 1.87 | 110 |
| 3 | 5.40 | 114 |
| 4 | 7.46 | 118 |
| 5 | 10.27 | 130.5 |
| 6 | 12.92 | 145 |
| 7 | 17.35 | 165 |
| 8 | 22.38 | 184 |
| 9 | 26.42 | 194 |
| 10 | 36.91 | 215 |
| 11 | 48.96 | 236 |
| 12 | 57.04 | 252 |
| 13 | 68.57 | 267 |

TABLE 12 (Cut VI)

73% (70% $AgNO_3$ + 30% $TlNO_3$) + 27% $KNO_3$ → $NaNO_3$

| Expt. No. | Mol.% $NaNO_3$ | Temp. of beginning of crystallization |
|---|---|---|
| 1 | 0 | 112° |
| 2 | 1.67 | 111.3 |
| 3 | 3.61 | 110 |
| 4 | 5.83 | 109 |
| 5 | 8.77 | 116.2 |
| 6 | 10.61 | 125 |
| 7 | 14.11 | 140.5 |
| 8 | 18.42 | 160 |
| 9 | 22.58 | 176.5 |
| 10 | 27.23 | 188 |
| 11 | 33.55 | 201 |
| 12 | 45.80 | 224 |
| 13 | 57.33 | 236 |
| 14 | 66.18 | 259 |
| 15 | 77.24 | 271 |
| 16 | 85.87 | 283.5 |
| 17 | 91.71 | 295 |

TABLE 13 (Cut VII)

20% (70% $AgNO_3$ + 30% $TlNO_3$) + 80% $KNO_3$ → $NaNO_3$

| Expt. No. | Mol.% $NaNO_3$ | Temp. of beginning of crystallization |
|---|---|---|
| 1 | 0 | 289° |
| 2 | 9.5 | 262 |
| 3 | 19.67 | 234 |
| 4 | 29.56 | 210.5 |
| 5 | 39.92 | 198.4 |
| 6 | 49.43 | 209 |
| 7 | 58.37 | 226 |
| 8 | 65.79 | 240 |
| 9 | 72.40 | 254 |
| 10 | 79.12 | 267 |
| 11 | 83.97 | 277 |
| 12 | 89.04 | 289 |

more sharply. The field of crystallization of the continuous solid solutions is further enlarged, and their separation is observed at a temperature of about 180°. The field of crystallization of the incongrous compound $AgNO_3 \cdot KNO_3$, which in the tetrahedral face system $AgNO_3$ – $KNO_3$ – $NaNO_3$ has a triangular form, here becomes quadrangular as a result of the internal angles of the field being formed by eutectic and peritectic lines. Thus the corners of the field $AgNO_3 \cdot KNO_3$ are ternary transition points. In the field of crystallization of $KNO_3$, in the neighborhood of the ternary point, there are lines of polymorphous transformation of $KNO_3$ (129°), and in the vicinity of the pure components $KNO_3$ and $NaNO_3$ there are lines of polymorphous transformation of the secondary variety (at 315° for $KNO_3$ and at 275° for $NaNO_3$).

The ternary transition points correspond: the first, to a temperature of 106° and composition 18.3% $TlNO_3$, 42.7% $AgNO_3$, 31% $KNO_3$ and 8% $NaNO_3$; the second, to a temperature of 109° and composition 20.7% $TlNO_3$, 48.3% $AgNO_3$, 23% $KNO_3$ and 8% $NaNO_3$.

Section III (56% $AgNO_3$ + 44% $TlNO_3$) — $KNO_3$ — $NaNO_3$. In investigating the given section there were studied: the pseudo-binary system (56% $AgNO_3$ + 44% $TlNO_3$) – $NaNO_3$ and the six following cuts:

I [90% (56% $AgNO_3$ + 44% $TlNO_3$) + 10% $NaNO_3$] → $KNO_3$,
II [80% (56% $AgNO_3$ + 44% $TlNO_3$) + 20% $NaNO_3$] → $KNO_3$,
III [65% (56% $AgNO_3$ + 44% $TlNO_3$) + 35% $NaNO_3$] → $KNO_3$,
IV [50% (56% $AgNO_3$ + 44% $TlNO_3$) + 50% $NaNO_3$] → $KNO_3$,
V [93% (56% $AgNO_3$ + 44% $TlNO_3$) + 7% $KNO_3$] → $NaNO_3$,
VI [86.57% (56% $AgNO_3$ + 44% $TlNO_3$) + 13.43% $KNO_3$] → $NaNO_3$.

The experimental figures are shown in Tables 14, 15, 16, 17, 18, 19, 20, respectively.

The resultant diagrams of the pseudo binary system (56% $AgNO_3$ + 44% $TlNO_3$) – $NaNO_3$ and the quaternary cuts of section III are given in Figs. 14 and 15.

The diagram of section III, summarizing all the experimental results of the section, is given in Fig. 16 as a triangular isotherm. Despite the general character of the diagram of section III it is still similar to the diagram of the tetrahedral face system $AgNO_3$ – $KNO_3$ –

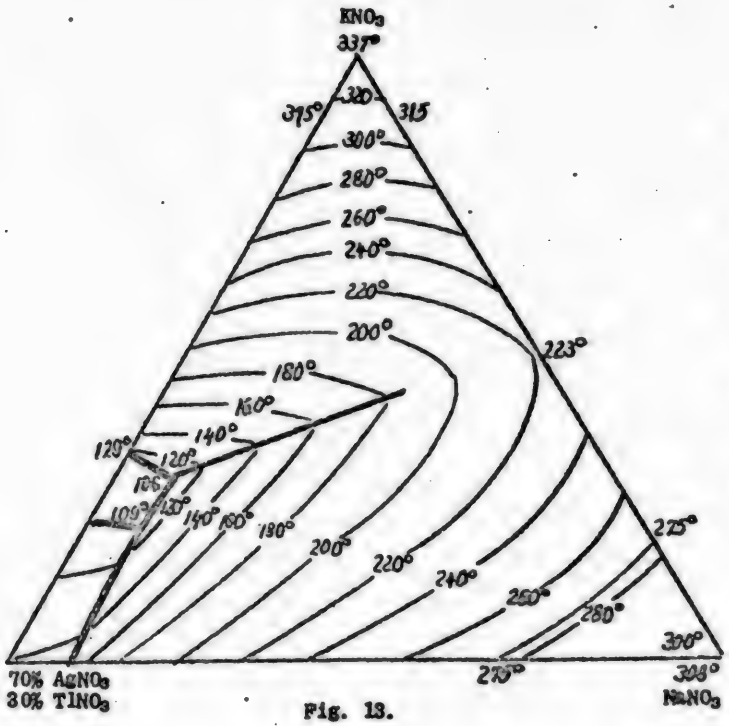


Fig. 13.

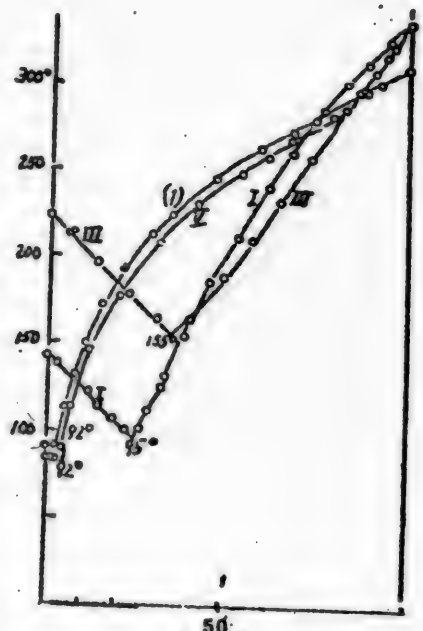


Fig. 14

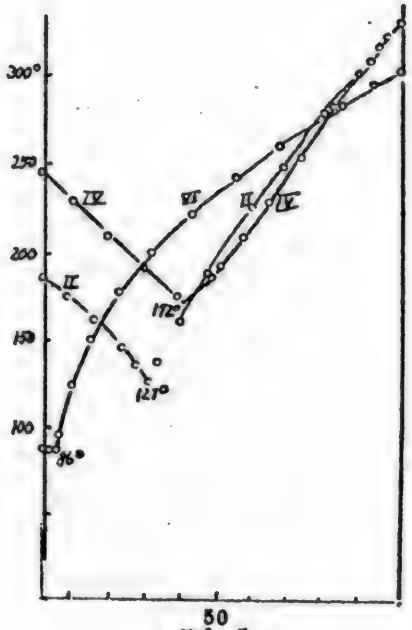


Fig. 15

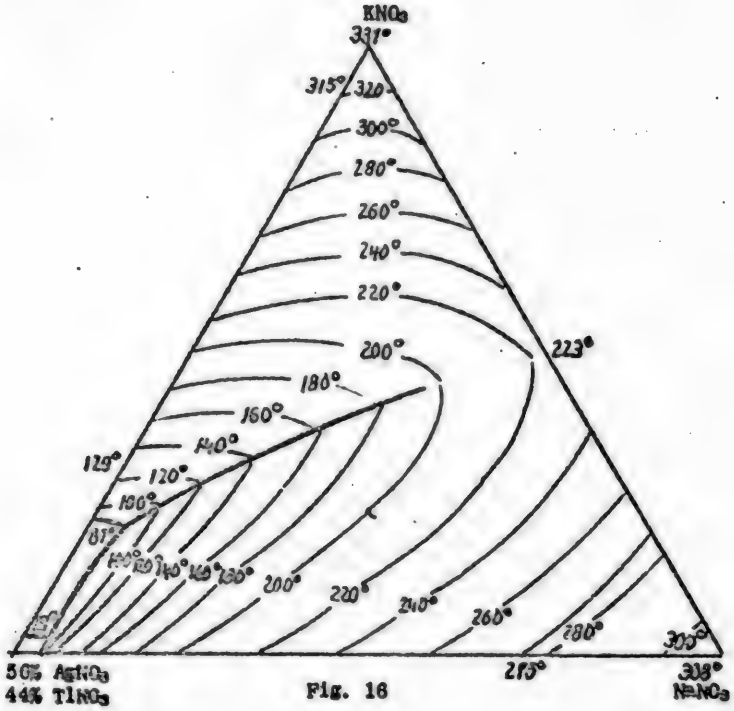


Fig. 16

TABLE 14

56% $AgNO_3$ + 44% $TlNO_3$ → $NaNO_3$

| Expt. No. | Mol.% $NaNO_3$ | Temp. of beginning of crystallization |
|---|---|---|
| 1 | 0 | 92° |
| 2 | 1.69 | 92 |
| 3 | 3.42 | 92 |
| 4 | 4.21 | 96 |
| 5 | 5.64 | 113 |
| 6 | 7.97 | 132 |
| 7 | 10.45 | 149 |
| 8 | 15.38 | 172 |
| 9 | 21.14 | 192 |
| 10 | 28.98 | 211 |
| 11 | 34.20 | 223 |
| 12 | 46.82 | 243.6 |
| 13 | 58.94 | 261 |
| 14 | 67.73 | 272 |
| 15 | 77.20 | 284 |
| 16 | 86.11 | 295 |

TABLE 15 (Cut I)

90% (56% $AgNO_3$ + 44% $TlNO_3$) + 10% $NaNO_3$ → $KNO_3$

| Expt. No. | Mol.% $KNO_3$ | Temp of beginning of crystallization |
|---|---|---|
| 1 | 0 | 142° |
| 2 | 2.60 | 137 |
| 3 | 7.97 | 127 |
| 4 | 11.13 | 120 |
| 5 | 14.48 | 113 |
| 6 | 18.04 | 105 |
| 7 | 22.35 | 99 |
| 8 | 25.30 | 98.7 |
| 9 | 28.29 | 110 |
| 10 | 31.84 | 123 |
| 11 | 33.61 | 130 |
| 12 | 38.52 | 154.5 |
| 13 | 45.35 | 183 |
| 14 | 53.16 | 209 |
| 15 | 61.22 | 238 |
| 16 | 68.02 | 257 |
| 17 | 76.34 | 282 |
| 18 | 82.97 | 298.5 |
| 19 | 88.63 | 310 |
| 20 | 94.57 | 324 |

TABLE 16 (Cut II)

80% (56% $AgNO_3$ + 44% $TlNO_3$) + 20% $NaNO_3$ → $KNO_3$

| Expt. No. | Mol.% $KNO_3$ | Temp. of beginning of crystallization |
|---|---|---|
| 1 | 0 | 188° |
| 2 | 7.00 | 176 |
| 3 | 14.48 | 162 |
| 4 | 22.01 | 148 |
| 5 | 27.06 | 137.5 |
| 6 | 30.11 | 128 |
| 7 | 32.99 | 138 |
| 8 | 39.71 | 162 |
| 9 | 49.93 | 197 |
| 10 | 59.17 | 227 |
| 11 | 66.81 | 251 |
| 12 | 78.63 | 282 |
| 13 | 88.25 | 304 |
| 14 | 96.02 | 326 |

TABLE 17 (Cut III)

65% (56% $AgNO_3$ + 44% $TlNO_3$) + 35% $NaNO_3$ → $KNO_3$

| Expt. No. | Mol.% $KNO_3$ | Temp. beginning of crystallization |
|---|---|---|
| 1 | 0 | 222.5° |
| 2 | 6.10 | 212 |
| 3 | 13.97 | 195 |
| 4 | 22.65 | 177 |
| 5 | 30.55 | 164 |
| 6 | 40.56 | 164 |
| 7 | 49.36 | 187.4 |
| 8 | 57.71 | 209 |
| 9 | 64.94 | 232 |
| 10 | 73.00 | 258 |
| 11 | 82.84 | 285 |
| 12 | 90.47 | 307 |
| 13 | 93.38 | 316 |
| 14 | 95.29 | 322.5 |

TABLE 18 (Cut IV)

50% (56% $AgNO_3$ + 44% $TlNO_3$) + 50% $NaNO_3$ → $KNO_3$

| Expt. No. | Mol.% $KNO_3$ | Temp. of beginning of crystallization |
|---|---|---|
| 1 | 0 | 248° |
| 2 | 8.60 | 232 |
| 3 | 18.01 | 212 |
| 4 | 27.35 | 195 |
| 5 | 37.35 | 176 |
| 6 | 46.77 | 190 |
| 7 | 55.65 | 212 |
| 8 | 62.31 | 232 |
| 9 | 71.12 | 257 |
| 10 | 81.52 | 285 |
| 11 | 91.89 | 311 |
| 12 | 96.77 | 326 |

TABLE 19 (Cut V)

93% (56% $AgNO_3$ + 44% $TlNO_3$) + 7% $KNO_3$ → $NaNO_3$

| Expt. No. | Mol.% $NaNO_3$ | Temp. of beginning of crystallization |
|---|---|---|
| 1 | 0 | 85.5° |
| 2 | 1.18 | 84.2 |
| 3 | 2.61 | 83.6 |
| 4 | 4.54 | 90 |
| 5 | 7.18 | 113.6 |
| 6 | 12.03 | 145 |
| 7 | 20.36 | 176 |
| 8 | 31.71 | 206 |
| 9 | 42.02 | 225 |
| 10 | 54.12 | 246 |
| 11 | 61.23 | 257 |
| 12 | 66.87 | 265 |
| 13 | 79.58 | 281 |
| 14 | 88.95 | 294 |

$NaNO_3$; but in this case the differences are expressed with still greater force. The field of continuous solid solutions ($KNO_3$ + $NaNO_3$) is enlarged a bit more. The separation of the continuous solid solutions ($KNO_3$ + $NaNO_3$) is observed at a temperature of about 180°. The field of crystallization of the compound $AgNO_3 \cdot KNO_3$ is strongly displaced toward the corner (56% $AgNO_3$ + 44% $TlNO_3$); it has a quadrangular form and stretches along the line (56% $AgNO_3$ + 44% $TlNO_3$) — $KNO_3$. The inner angles of this field represent ternary transition points of the given section. There are two such points: One corresponds to a temperature of 85° and

TABLE 20

(Cut VI)

$$86.57\%\ (56\%\ AgNO_3 + 44\%\ TlNO_3) \\ 13.43\%\ KNO_3 \Big\} \longrightarrow NaNO_3$$

| Expt. No. | Mol.% $NaNO_3$ | Temp. of beginning of crystallization |
|---|---|---|
| 1 | 0 | 88° |
| 2 | 1.66 | 87.2 |
| 3 | 3.21 | 84 |
| 4 | 5.74 | 95 |
| 5 | 9.29 | 124 |
| 6 | 13.63 | 149.5 |
| 7 | 19.44 | 164 |
| 8 | 21.16 | 178 |
| 9 | 30.29 | 200.4 |
| 10 | 41.57 | 223 |
| 11 | 52.82 | 246 |
| 12 | 65.03 | 263 |
| 13 | 82.32 | 285 |
| 14 | 92.03 | 300 |

the composition 31.7% $TlNO_3$, 40.3% $AgNO_3$, 22% $KNO_3$ and 6% $NaNO_3$; the other to 79° and a composition of 41% $TlNO_3$, 52.2% $AgNO_3$, 3% $KNO_3$, and 3.8% $NaNO_3$. We can observe the presence of the line of polymorphous transformation of $KNO_3$ (129°) and the lines of polymorphous transformation of the second variety of $KNO_3$ (315°) and $NaNO_3$ (275°).

It was previously noted (in the description of the ternary system $TlNO_3$ — $AgNO_3$ — $KNO_3$) that the melts in the region of crystallization of the incongruous compound show much greater viscosity; this greatly increased viscosity was also observed during the investigation of quaternary melts situated in the region of crystallization of the incongruous compound $AgNO_3 \cdot KNO_3$.

Section IV (50% $AgNO_3$ + 50% $TlNO_3$) — $KNO_3$ — $NaNO_3$.

Section IV, made through the maximum of the congruent compound $TlNO_3 \cdot AgNO_3$, represents an independent ternary system, $TlNO_3 \cdot AgNO_3$ - $KNO_3$ - $NaNO_3$.

For the study of this section, the following 6 cuts were made:

I [96% (50% $AgNO_3$ + 50% $TlNO_3$) + 4% $KNO_3$] → $NaNO_3$.
II [89% (50% $AgNO_3$ + 50% $TlNO_3$) + 11% $KNO_3$] → $NaNO_3$.
III [82% (50% $AgNO_3$ + 50% $TlNO_3$) + 18% $KNO_3$] → $NaNO_3$.
IV [65% (50% $AgNO_3$ + 50% $TlNO_3$) + 35% $KNO_3$] → $NaNO_3$.
V [50% (50% $AgNO_3$ + 50% $TlNO_3$) + 50% $KNO_3$] → $NaNO_3$.
VI [40% (50% $AgNO_3$ + 50% $TlNO_3$) + 60% $NaNO_3$] → $KNO_3$.

TABLE 21

(Cut I)

$$96\%\ (50\%\ AgNO_3 + 50\%\ TlNO_3) \\ 4\%\ KNO_3 \Big\} \longrightarrow NaNO_3$$

| Expt. No. | Mol.% $NaNO_3$ | Temp. of beginning of crystallization |
|---|---|---|
| 1 | 0 | 84° |
| 2 | 1.35 | 84 |
| 3 | 2.93 | 84 |
| 4 | 4.79 | 88 |
| 5 | 7.13 | 118 |
| 6 | 11.63 | 144 |
| 7 | 19.44 | 174 |
| 8 | 27.11 | 197 |
| 9 | 34.42 | 216 |
| 10 | 44.08 | 232 |
| 11 | 53.99 | 248 |
| 12 | 63.35 | 260 |
| 13 | 73.47 | 271 |
| 14 | 82.94 | 286 |

TABLE 22

(Cut II)

$$89\%\ (50\%\ AgNO_3 + 50\%\ TlNO_3) \\ 11\%\ KNO_3 \Big\} \longrightarrow NaNO_3$$

| Expt. No. | Mol.% $NaNO_3$ | Temp. of beginning of crystallization |
|---|---|---|
| 1 | 0 | 87° |
| 2 | 1.25 | 88 |
| 3 | 2.72 | 89 |
| 4 | 4.37 | 89.5 |
| 5 | 6.64 | 96.5 |
| 6 | 10.87 | 128 |
| 7 | 18.27 | 164 |
| 8 | 28.65 | 191.5 |
| 9 | 39.60 | 213 |
| 10 | 52.49 | 235 |
| 11 | 69.28 | 263 |
| 12 | 84.66 | 285 |

TABLE 23

(Cut III)

$$82\%\ (50\%\ AgNO_3 + 50\%\ TlNO_3) \\ 18\%\ KNO_3 \Big\} \longrightarrow NaNO_3$$

| Expt. No. | Mol.% $NaNO_3$ | Temp. of beginning of crystallization |
|---|---|---|
| 1 | 0 | 90° |
| 2 | 1.16 | 91.3 |
| 3 | 2.51 | 92.5 |
| 4 | 4.04 | 94 |
| 5 | 6.15 | 96.6 |
| 6 | 8.02 | 106 |
| 7 | 10.10 | 119 |
| 8 | 17.08 | 153 |
| 9 | 28.22 | 189 |
| 10 | 43.44 | 217 |
| 11 | 53.32 | 238 |
| 12 | 64.97 | 258 |
| 13 | 72.91 | 268.4 |
| 14 | 83.42 | 285 |
| 15 | 91.24 | 297.5 |

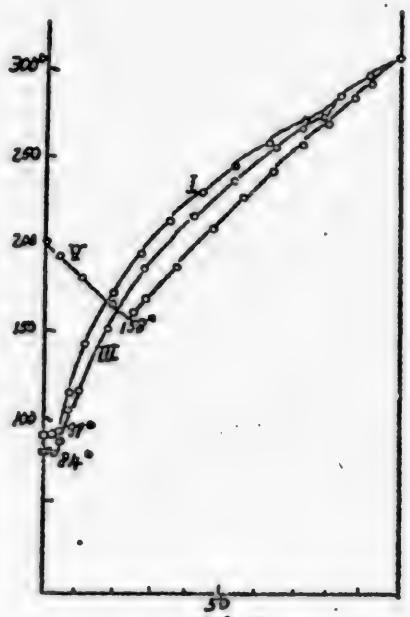


Fig. 17

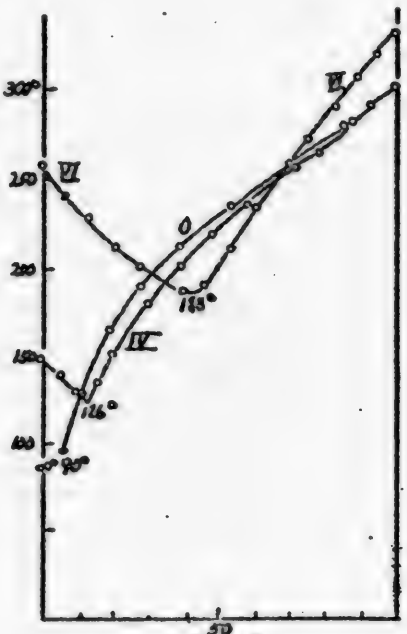


Fig. 18

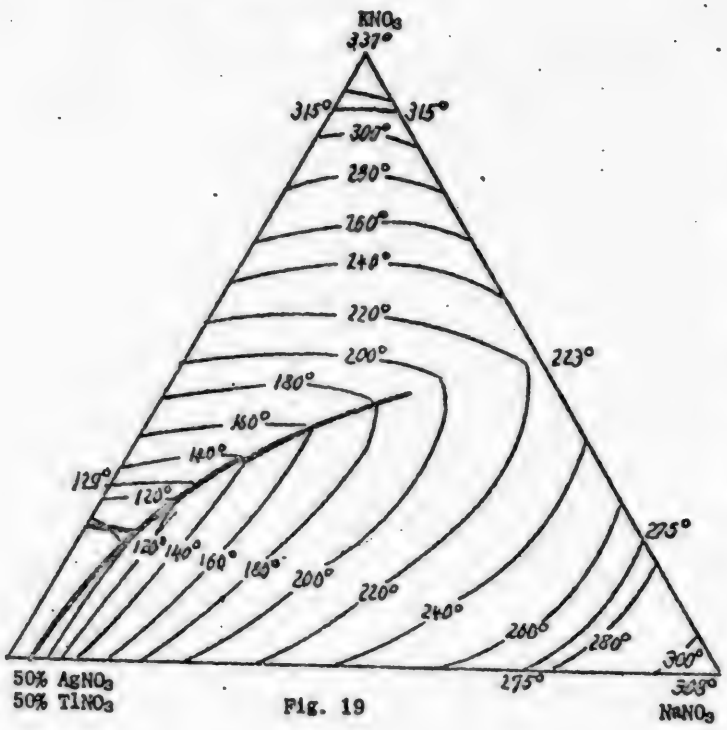


Fig. 19

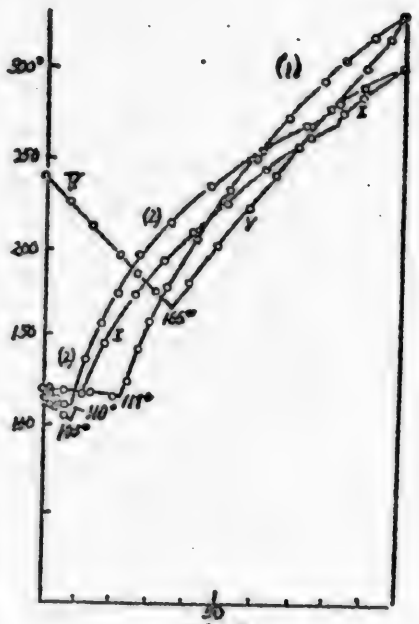


Fig. 20

TABLE 24

(Cut IV)

65%(50% $AgNO_3$+50% $TlNO_3$) / 35% $KNO_3$ → $NaNO_3$

| Expt. No. | Mol.% $NaNO_3$ | Temp. of beginning of crystallization |
|---|---|---|
| 1 | 0 | 151° |
| 2 | 4.15 | 142 |
| 3 | 11.50 | 130 |
| 4 | 16.03 | 137 |
| 5 | 20.62 | 153.4 |
| 6 | 30.22 | 183 |
| 7 | 39.38 | 202 |
| 8 | 49.35 | 220 |
| 9 | 58.46 | 235 |
| 10 | 71.72 | 259 |
| 11 | 77.93 | 268.5 |
| 12 | 86.44 | 284 |
| 13 | 92.81 | 297 |

TABLE 25

(Cut V)

50%(50%$AgNO_3$+50%$TlNO_3$) / 50% $KNO_3$ → $NaNO_3$

| Expt. No. | Mol.% $NaNO_3$ | Temp. of beginning of crystallization |
|---|---|---|
| 1 | 0 | 204° |
| 2 | 4.12 | 195 |
| 3 | 10.71 | 181 |
| 4 | 19.34 | 167 |
| 5 | 24.73 | 162.5 |
| 6 | 28.56 | 170 |
| 7 | 37.48 | 188.5 |
| 8 | 47.35 | 209.5 |
| 9 | 56.50 | 227 |
| 10 | 64.32 | 243 |
| 11 | 72.47 | 258 |
| 12 | 79.82 | 269 |
| 13 | 87.64 | 284 |
| 14 | 92.21 | 293 |

TABLE 26

(Cut VI)

40%(50%$AgNO_3$+50%$TlNO_3$) / 60% $KNO_3$ → $KNO_3$

| Expt. No. | Mol.% $KNO_3$ | Temp. of beginning of crystallization |
|---|---|---|
| 1 | 0 | 260° |
| 2 | 7.21 | 244 |
| 3 | 13.23 | 231 |
| 4 | 21.65 | 214 |
| 5 | 27.92 | 204 |
| 6 | 34.51 | 194 |
| 7 | 39.93 | 190 |
| 8 | 47.01 | 193 |
| 9 | 53.95 | 212 |
| 10 | 61.23 | 235 |
| 11 | 67.89 | 254 |
| 12 | 77.02 | 276 |
| 13 | 84.12 | 295 |
| 14 | 90.43 | 309 |
| 15 | 95.96 | 324 |

The experimental results of the quaternary cuts are given in Tables 23, 22, 23, 24, 25 and 26.

The diagrams of the cuts are shown in Figs. 17, 18.

The experimental results of Section IV are summarized in the diagram shown in Fig. 19 as a triangular isotherm.

The diagram of Section IV (which is an independent ternary system) consists principally of two fields of crystallization: a small field of the compound $TlNO_3 \cdot AgNO_3$, and the field of crystallization of continuous solid solutions $KNO_3$ + $NaNO_3$. At a temperature near 189°, the continuous solid solutions separate, and the separate parts formed in this way near the field $TlNO_3 \cdot AgNO_3$ may be regarded as fields of crystallization of $KNO_3$ and $NaNO_3$.

Through the field of crystallization of $KNO_3$ passes the line of polymorphous transformation of $KNO_3$ (129°). Near the corners $KNO_3$ and $NaNO_3$ are the lines of the polymorphous transformation of the second variety of $KNO_3$ (315°) and $NaNO_3$ (275°). The diagram of the section has one ternary transition point with a temperature of 105° and a composition of 35% $TlNO_3$, 35% $AgNO_3$, 22% $KNO_3$ and 8% $NaNO_3$.

Section V (35% $AgNO_3$ + 65% $TlNO_3$) — $KNO_3$ — $NaNO_3$.

In the study of the Vth section, two constituent pseudo binary systems were investigated, and the following 6 quaternary cuts:

I [85% (35% $AgNO_3$ + 65% $TlNO_3$) + 15% $KNO_3$] → $NaNO_3$,

II [75% (35% $AgNO_3$ + 65% $TlNO_3$) + 25% $KNO_3$] → $NaNO_3$,

III [65% (35% $AgNO_3$ + 65% $TlNO_3$) + 35% $KNO_3$] → $NaNO_3$,

IV [92% (35% $AgNO_3$ + 65% $TlNO_3$) + 8% $NaNO_3$] → $KNO_3$,

V [50% (35% $AgNO_3$ + 65% $TlNO_3$) + 50% $NaNO_3$] → $KNO_3$,

VI [30% (35% $AgNO_3$ + 65% $TlNO_3$) + 70% $NaNO_3$] → $KNO_3$.

The experimental figures of the pseudo binary systems (35% $AgNO_3$ + 65% $TlNO_3$) — $KNO_3$, and (35% $AgNO_3$ + 65% $TlNO_3$) — $NaNO_3$ and the quaternary cuts are given in Tables 27, 28, 29, 30, 31, 32, 33, and 34.

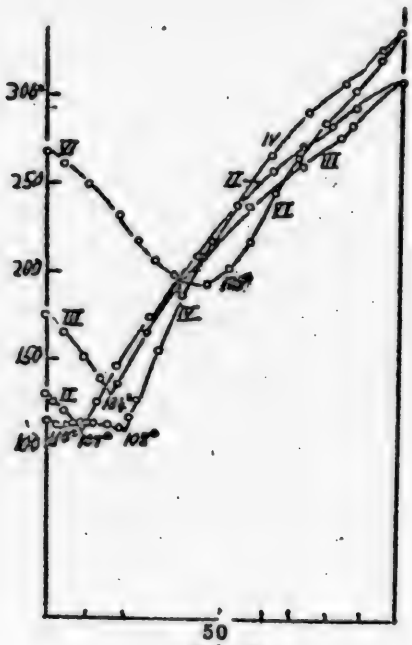


Fig. 21

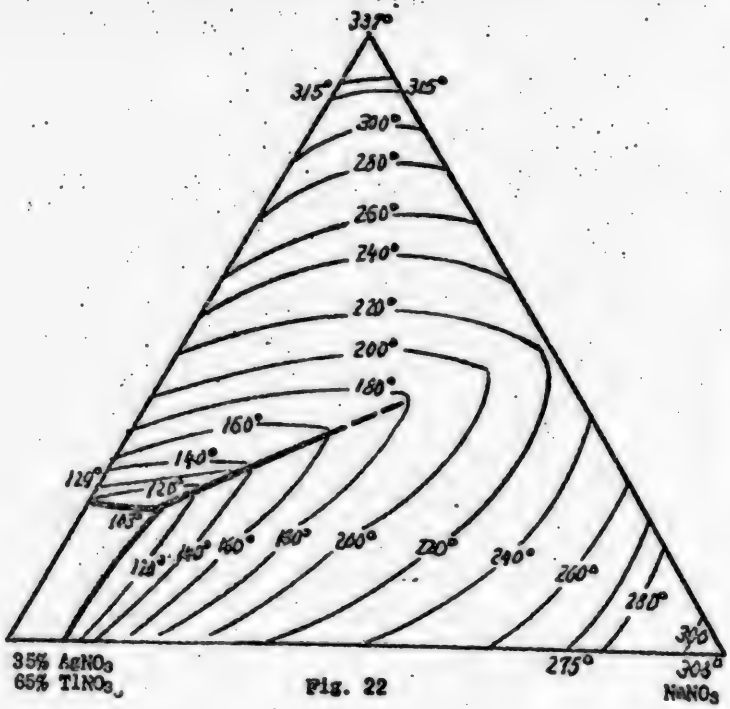


Fig. 22

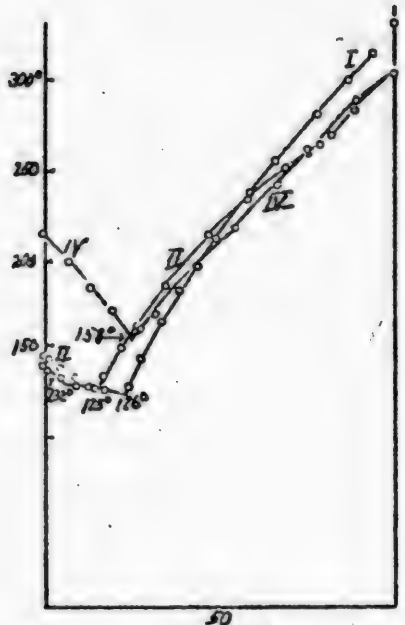


Fig. 23

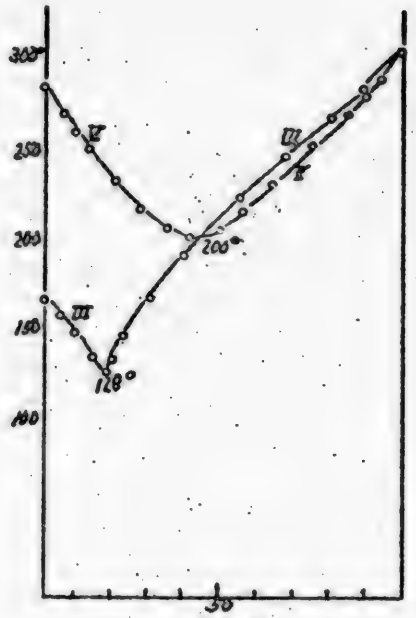


Fig. 24

TABLE 27

35% $AgNO_3$
65% $TlNO_3$ → $KNO_3$

| Expt. No. | Mol.% $KNO_3$ | Temp. of beginning of crystallization |
|---|---|---|
| 1 | 0 | 120° |
| 2 | 6.86 | 119.4 |
| 3 | 13.43 | 118.6 |
| 4 | 20.92 | 117.4 |
| 5 | 23.87 | 127 |
| 6 | 26.95 | 144 |
| 7 | 29.98 | 159 |
| 8 | 35.01 | 178 |
| 9 | 42.94 | 207 |
| 10 | 52.03 | 235 |
| 11 | 58.77 | 254 |
| 12 | 67.48 | 277 |
| 13 | 77.32 | 299 |
| 14 | 82.51 | 309 |
| 15 | 90.89 | 324 |

TABLE 28

35% $AgNO_3$
65% $TlNO_3$ → $NaNO_3$

| Expt. No. | Mol.% $NaNO_3$ | Temp. of beginning of crystallization |
|---|---|---|
| 1 | 0 | 120° |
| 2 | 2.32 | 118 |
| 3 | 4.71 | 115 |
| 4 | 7.02 | 110.5 |
| 5 | 9.07 | 116 |
| 6 | 11.83 | 137 |
| 7 | 15.94 | 158 |
| 8 | 19.65 | 175 |
| 9 | 25.89 | 196 |
| 10 | 34.97 | 217 |
| 11 | 45.08 | 236.5 |
| 12 | 59.12 | 258 |
| 13 | 71.48 | 273 |
| 14 | 81.15 | 286.5 |
| 15 | 88.09 | 297 |

TABLE 29 (Cut I)

85%(35%$AgNO_3$+65%$TlNO_3$)
15% $KNO_3$ → $NaNO_3$

| Expt. No. | Mol.% $NaNO_3$ | Temp. of beginning of crystallization |
|---|---|---|
| 1 | 0 | 118° |
| 2 | 2.82 | 115.5 |
| 3 | 4.31 | 111 |
| 4 | 7.23 | 107 |
| 5 | 11.70 | 119 |
| 6 | 17.98 | 148.4 |
| 7 | 25.91 | 178 |
| 8 | 34.39 | 195 |
| 9 | 42.57 | 212 |
| 10 | 51.13 | 230 |
| 11 | 61.92 | 249 |
| 12 | 73.83 | 265 |
| 13 | 83.24 | 281.5 |
| 14 | 89.37 | 290.5 |

TABLE 30
(Cut II)

75%(35%$AgNO_3$+65%$TlNO_3$)
25% $KNO_3$ → $NaNO_3$

| Expt. No. | Mol.% $NaNO_3$ | Temp. of beginning of crystallization |
|---|---|---|
| 1 | 0 | 129° |
| 2 | 2.62 | 124 |
| 3 | 4.78 | 120 |
| 4 | 7.89 | 113 |
| 5 | 10.93 | 102.5 |
| 6 | 14.01 | 125.5 |
| 7 | 19.63 | 145 |
| 8 | 29.12 | 172 |
| 9 | 42.07 | 207 |
| 10 | 53.72 | 235 |
| 11 | 63.24 | 254 |
| 12 | 71.97 | 268 |
| 13 | 79.99 | 281 |
| 14 | 86.75 | 291.5 |

TABLE 31
(Cut III)

65%(35%$AgNO_3$+65%$TlNO_3$)
35% $KNO_3$ → $NaNO_3$

| Expt. No. | Mol.% $NaNO_3$ | Temp. of beginning of crystallization |
|---|---|---|
| 1 | 0 | 176° |
| 2 | 4.23 | 164 |
| 3 | 10.00 | 120 |
| 4 | 14.92 | 140 |
| 5 | 18.53 | 136 |
| 6 | 27.55 | 165 |
| 7 | 35.79 | 1911 |
| 8 | 43.64 | 209 |
| 9 | 57.02 | 236 |
| 10 | 71.94 | 259 |
| 11 | 81.58 | 276 |
| 12 | 85.27 | 282.5 |

TABLE 32
(Cut IV)

92%(35%$AgNO_3$+65%$TlNO_3$)
8% $NaNO_3$ → $KNO_3$

| Expt. No. | Mol.% $KNO_3$ | Temp. of beginning of crystallization |
|---|---|---|
| 1 | 0 | 113° |
| 2 | 2.21 | 111.5 |
| 3 | 4.72 | 110.4 |
| 4 | 8.67 | 111.5 |
| 5 | 12.50 | 112 |
| 6 | 17.52 | 110 |
| 7 | 20.95 | 108.5 |
| 8 | 23.84 | 115 |
| 9 | 25.79 | 124 |
| 10 | 31.81 | 154 |
| 11 | 39.57 | 184.5 |
| 12 | 42.29 | 209 |
| 13 | 53.64 | 235.5 |
| 14 | 63.02 | 264 |
| 15 | 73.48 | 287 |
| 16 | 83.11 | 305.5 |
| 17 | 93.24 | 325 |

Diagrams of the pseudo binary systems and the quaternary cuts are shown in Figs. 20 and 21.

The experimental results of Section V are summarized in the diagram, shown in Fig.22 as a triangular isotherm. The diagram of Section V, like the diagram of Section VI, is basically similar to the diagram of the tetrahedral surface system $TlNO_3$ — $KNO_3$ — $NaNO_3$.

There is a difference in the greater field of crystallization and in the temperature of

TABLE 33
(Cut V)

50% (35% $AgNO_3$ + 65% $TlNO_3$ / 50% $NaNO_3$) → $KNO_3$

| Expt. No. | Mol. % $KNO_3$ | Temp. of beginning of crystallization |
|---|---|---|
| 1 | 0 | 243° |
| 2 | 7.20 | 228 |
| 3 | 18.85 | 214 |
| 4 | 21.42 | 197.5 |
| 5 | 26.53 | 187 |
| 6 | 32.01 | 176.5 |
| 7 | 37.15 | 172 |
| 8 | 40.83 | 182 |
| 9 | 49.70 | 203 |
| 10 | 57.22 | 224 |
| 11 | 65.03 | 244 |
| 12 | 71.82 | 263 |
| 13 | 79.93 | 282.5 |
| 14 | 89.37 | 306 |
| 15 | 95.88 | 322 |

TABLE 34
(Cut VI)

30% (35% $AgNO_3$ + 65% $TlNO_3$ / 70% $NaNO_3$) → $KNO_3$

| Expt. No. | Mol.% $KNO_3$ | Temp. of beginning of crystallization |
|---|---|---|
| 1 | 0 | 268° |
| 2 | 4.97 | 261 |
| 3 | 11.29 | 250 |
| 4 | 19.98 | 231 |
| 5 | 25.18 | 218 |
| 6 | 29.89 | 207 |
| 7 | 35.71 | 196 |
| 8 | 45.02 | 194 |
| 9 | 51.15 | 203.5 |
| 10 | 58.78 | 218 |
| 11 | 64.35 | 245 |
| 12 | 70.85 | 265 |
| 13 | 78.68 | 286 |
| 14 | 86.71 | 304 |
| 15 | 94.95 | 320 |

separation in the solid solutions ($KNO_3$ + $NaNO_3$). In the diagram of Section V, the field of crystallization of $TlNO_3$ is very small, and the field of crystallization of the continuous solid solutions significantly less than in the system $TlNO_3$ — $KNO_3$ — $NaNO_3$. The separation of the continuous solid solutions ($KNO_3$ + $NaNO_3$) is observed at a temperature of about 170°. In view of the separation of the continuous solid solutions ($KNO_3$ + $NaNO_3$) in the vicinity of the field of crystallization of $TlNO_3$, separate fields are formed, and these may be regarded as fields of crystallization of $KNO_3$ and $NaNO_3$. Just as in the case of the previous section, there are lines corresponding to the polymorphous transformations of $KNO_3$ (129°) and of the second variety of $KNO_3$ (315°) and $NaNO_3$ (275°). In the diagram of Section V, there is one ternary point, corresponding to a temperature of 103° and a composition of 44.85%, etc.

Section VI (20% $AgNO_3$ + 80% $TlNO_3$) — $KNO_3$ — $NaNO_3$.

For the investigation of Section VI, the following 5 cuts were studied:

I [85% (20% $AgNO_3$ + 80% $TlNO_3$) + 15% $NaNO_3$] → $KNO_3$.

II [80% (20% $AgNO_3$ + 80% $TlNO_3$) + 20% $KNO_3$] → $NaNO_3$.

III [70% (20% $AgNO_3$ + 80% $TlNO_3$) + 30% $KNO_3$] → $NaNO_3$.

IV [55% (20% $AgNO_3$ + 80% $TlNO_3$) + 45% $KNO_3$] → $NaNO_3$.

V [25% (20% $AgNO_3$ + 80% $TlNO_3$) + 75% $KNO_3$] → $NaNO_3$.

The experimental results of Section VI are presented in Tables 35, 36, 37, 38, and 39, respectively.

Diagrams of the cuts are shown in Figs. 23 and 24.

The diagram of Section VI (Fig. 25) in which the experimental results of the VIth Section are summarized, is still more reminiscent than the diagram of Section V, of the diagram of the tetrahedral surface system $TlNO_3$— $KNO_3$ —$NaNO_3$. The fields of crystallization of $TlNO_3$ and

**TABLE 35**

**(Cut I)**

85% (20% $AgNO_3$ + 80% $TlNO_3$) + 15% $NaNO_3$ → $KNO_3$

| Expt. No. | Mol.% $KNO_3$ | Temp. of Beginning of crystallization |
|---|---|---|
| 1 | 0 | 142° |
| 2 | 2.42 | 140 |
| 3 | 5.01 | 134 |
| 4 | 9.71 | 131 |
| 5 | 14.97 | 129.5 |
| 6 | 17.37 | 128 |
| 7 | 24.23 | 131 |
| 8 | 27.93 | 146 |
| 9 | 34.12 | 168 |
| 10 | 39.26 | 185 |
| 11 | 49.18 | 215 |
| 12 | 58.28 | 240 |
| 13 | 65.93 | 258 |
| 14 | 77.85 | 286 |
| 15 | 87.02 | 304 |
| 16 | 93.29 | 318 |

**TABLE 36**

**(Cut II)**

80% (20% $AgNO_3$ + 80% $TlNO_3$) + 20% $KNO_3$ → $NaNO_3$

| Expt. No. | Mol.% $NaNO_3$ | Temp. of beginning of crystallization |
|---|---|---|
| 1 | 0 | 148° |
| 2 | 2.64 | 143.5 |
| 3 | 5.71 | 140 |
| 4 | 9.32 | 136 |
| 5 | 13.15 | 129 |
| 6 | 17.53 | 135 |
| 7 | 22.27 | 151 |
| 8 | 26.74 | 164 |
| 9 | 34.81 | 189 |
| 10 | 47.18 | 217 |
| 11 | 58.11 | 236 |
| 12 | 68.96 | 255 |
| 13 | 77.99 | 268 |
| 14 | 88.04 | 286 |

**TABLE 37**

**(Cut III)**

70% (20% $AgNO_3$ + 80% $TlNO_3$) + 30% $KNO_3$ → $NaNO_3$

| Expt. No. | Mol.% $NaNO_3$ | Temp. of beginning of crystallization |
|---|---|---|
| 1 | 0 | 168° |
| 2 | 4.03 | 158 |
| 3 | 8.18 | 149 |
| 4 | 13.79 | 136 |
| 5 | 18.11 | 135 |
| 6 | 22.24 | 149 |
| 7 | 29.87 | 169.5 |
| 8 | 39.53 | 193 |
| 9 | 54.41 | 225 |
| 10 | 67.27 | 250 |
| 11 | 80.02 | 270 |
| 12 | 89.64 | 286 |

**TABLE 38**

**(Cut IV)**

55% (20% $AgNO_3$ + 80% $TlNO_3$) + 45% $KNO_3$ → $NaNO_3$

| Expt. No. | Mol.% $NaNO_3$ | Temp. of beginning of crystallization |
|---|---|---|
| 1 | 0 | 216° |
| 2 | 7.18 | 200 |
| 3 | 13.84 | 185 |
| 4 | 29.86 | 171 |
| 5 | 27.91 | 161.5 |
| 6 | 32.01 | 171 |
| 7 | 44.11 | 198.5 |
| 8 | 54.98 | 220 |
| 9 | 67.04 | 244 |
| 10 | 75.37 | 260 |
| 11 | 81.65 | 271 |
| 12 | 88.12 | 287 |

**TABLE 39**

**(Cut V)**

25% (20% $AgNO_3$ + 80% $TlNO_3$) + 75% $KNO_3$ → $NaNO_3$

| oxpt. no. | Mol.% $NaNO_3$ | Temp. of beginning of crystallization. |
|---|---|---|
| 1 | 0 | 298° |
| 2 | 6.03 | 271.5 |
| 3 | 9.37 | 261 |
| 4 | 12.91 | 252 |
| 5 | 19.97 | 233.5 |
| 6 | 27.69 | 218 |
| 7 | 34.72 | 207 |
| 8 | 40.84 | 201 |
| 9 | 49.45 | 208 |
| 10 | 55.58 | 218 |
| 11 | 63.97 | 232 |
| 12 | 75.02 | 254 |
| 13 | 84.95 | 271 |
| 14 | 89.88 | 281.5 |
| 15 | 94.12 | 292 |

of the continuous solid solutions ($KNO_3$ + $NaNO_3$) yield in size to the corresponding fields of the surface system $TlNO_3$ — $KNO_3$ — $NaNO_3$, but at the same time surpass the corresponding fields of Section V.

The separation of the solid solutions takes place at a temperature of about 165°.

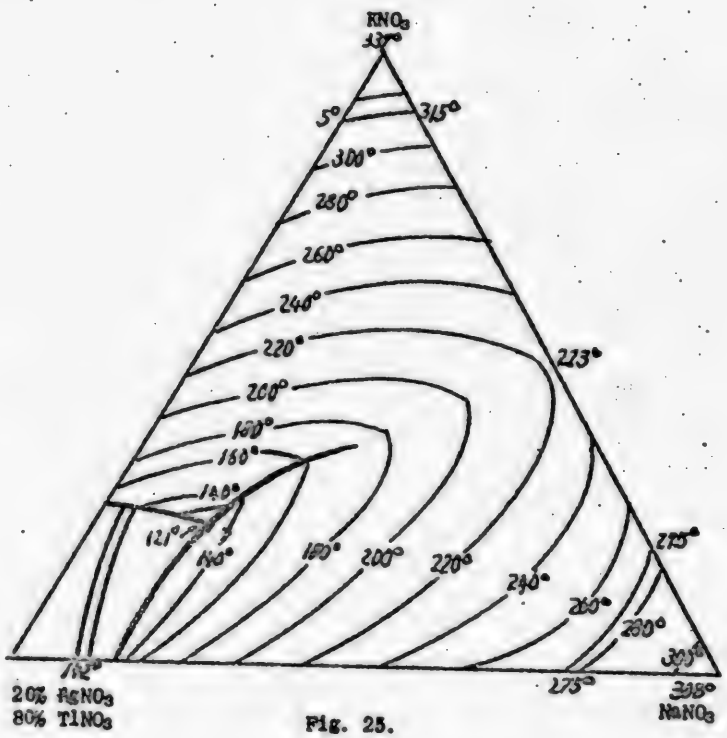


Fig. 25.

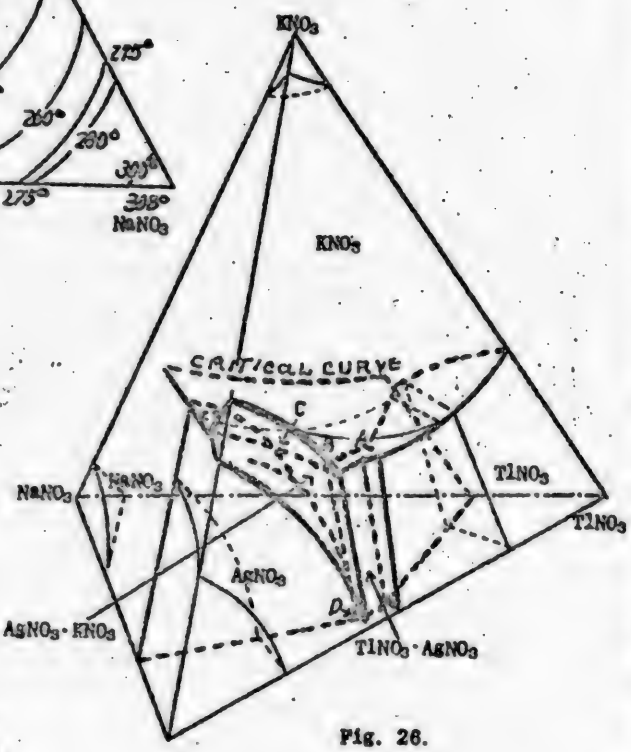


Fig. 26.

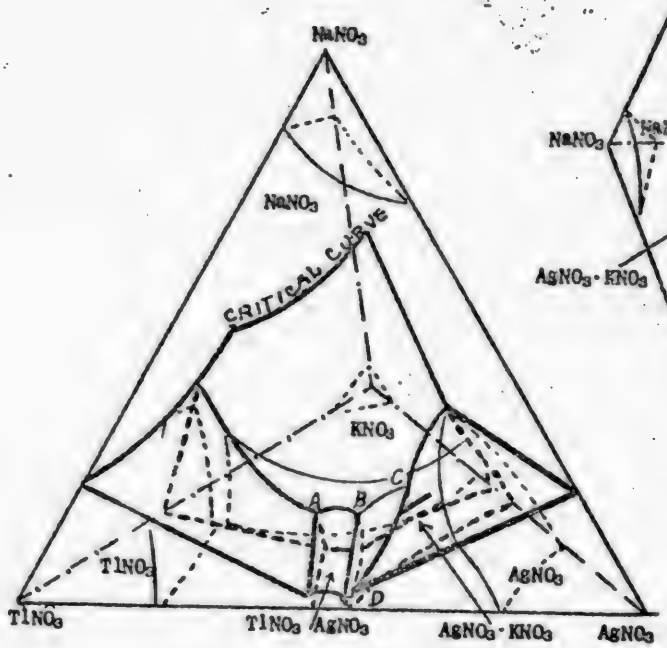


Fig. 27

Through the field of crystallization of $TlNO_3$ there passes the line of polymorphous transformation of $TlNO_3$ (142°); through the $KNO_3$ field, the line of transformation of $KNO_3$ (129°); and in the vicinity of the $KNO_3$ and $NaNO_3$ corners there pass the lines of polymorphous transformation of the second variety of $KNO_3$ (315°) and of $NaNO_3$ (275°).

The ternary point lies at a temperature of 121° and a composition of 48.8% $TlNO_3$, 12.2% $AgNO_3$, 23.6% $KNO_3$ and 16.4% $NaNO_3$.

## CONCLUSIONS

As a result of investigations carried out on the quaternary system $TlNO_3$ — $AgNO_3$ — $KNO_3$ — $NaNO_3$, a generalized liquidus diagram has been obtained. This diagram is the projection of several imaginary four dimensional figures upon the tetrahedron showing the composition of our system. The diagram of our system, Tl, Ag, K, Na $||NO_3$, is represented by a regular tetrahedron, each point at a corner, edge, face, or within it corresponding to a definite composition, determined by the components of the system and the temperature at which the melt of the given composition is in equilibrium with the solid phase. The diagram is presented in the form of a wired model, shown schematically in Figs. 26 and 27.

As is shown in the investigation of the internal sections, no quaternary chemical compounds exist in our system, and therefore the number and character of the phases (with regard to the volumes of crystallization) in the general diagram are determined by the diagrams of the four constituent tetrahedral face systems.

Our diagram consists of the following volumes of crystallization: 1) $TlNO_3$, 2) $AgNO_3$, 3) the congruent chemical compound $TlNO_3 \cdot AgNO_3$, 4) $KNO_3$, 5) the incongruent chemical compound $AgNO_3 \cdot KNO_3$, 6) $NaNO_3$, 7) the continuous solid solutions $KNO_3$ + $NaNO_3$.

All the volumes of crystallization enumerated are limited by corresponding surfaces of joint crystallization, as is graphically shown in the wired model and is obvious in Figs. 26 and 27.

The volumes of crystallization of $TlNO_3$ and $AgNO_3$ are approximately equal to each other in size, and both are smaller than the volumes of crystallization of $KNO_3$ and $NaNO_3$. The volumes of crystallization of the chemical compounds are comparatively small.

The volume of crystallization of the congruent compound $TlNO_3 \cdot AgNO_3$ (smallest of all) has the form of a long irregular four-faced prism.

The volume of crystallization of the incongruous compound $AgNO_3 \cdot KNO_3$ is fairly significant, and has an irregular drawn out form; it widens considerably, and approaches the volume of crystallization of the compound $TlNO_3 \cdot AgNO_3$.

In the vicinity of the corners $KNO_3$ and $NaNO_3$, the volume of crystallization corresponds to the continuous solid solutions $KNO_3$ + $NaNO_3$, separated by a critical curve representing the separation of these solid solutions.

The diagram of the system has two quaternary transition points (A and B), the quaternary point of intersection (C) and the quaternary eutectic point (D). (Compare Figs. 26 and 27, models of the diagram.) At point A the volumes of crystallization of $TlNO_3$, $KNO_3$, $NaNO_3$ and the compound $TlNO_3 \cdot AgNO_3$ all meet. At point B the volumes of crystallization of $KNO_3$, $NaNO_3$, the compound $AgNO_3 \cdot KNO_3$ and the compound $TlNO_3 \cdot AgNO_3$ meet.

At point C the volumes of crystallization of $AgNO_3$, $KNO_3$, $NaNO_3$ and the compound $AgNO_3 \cdot KNO_3$ meet.

At the quaternary eutectic point D the volumes of crystallization of $AgNO_3$, $NaNO_3$, the compound $AgNO_3 \cdot KNO_3$ and the compound $TlNO_3 \cdot AgNO_3$ meet.

The temperature and composition of the quaternary points of the components are shown in Table 40.

The influence of the melting points of the components is reflected in the general character of the diagrams of the quaternary system Tl, Ag, K, Na ||$NO_3$ and in the sizes of the volumes: the highest melting components correspond to the greatest volumes of crystallization and vice versa. The closeness of the melting points of thallium and silver nitrates (206 and 208°) results in a certain symmetry of the diagram and is reflected especially in the similar size of their volumes of crystallization and their symmetrical situation with regard to the volume of crystallization of the compound $TlNO_3 \cdot AgNO_3$.

TABLE 40

| Quaternary Points | Temperature | Mol. percent | | | |
|---|---|---|---|---|---|
| | | $TlNO_3$ | $AgNO_3$ | $KNO_3$ | $NaNO_3$ |
| A | 94° | 42.2 | 29 | 21 | 7.8 |
| B | 85 | 30.9 | 39.8 | 21.4 | 7.9 |
| C | 107 | 17.7 | 43.0 | 31.3 | 8 |
| D | 76 | 45.8 | 52 | 0.5 | 1.7 |

The compound $TlNO_3 \cdot AgNO_3$, with a small volume of crystallization and the lowest melting point (83°), so to speak draws the other four components of the system along the paths of crystallization which lead to the quaternary points, limiting the volume of crystallization of this compound.

The influence of this low temperature portion of the diagram is expressed to a special degree in the character of the volume of crystallization of the incongruous compound $AgNO_3 \cdot KNO_3$: It was observed above that the volume of crystallization of the incongrous compound, broadening considerably, passes over to the low temperature volume of crystallization of the compound $TlNO_3 \cdot AgNO_3$, i.e., here under the influence of the low temperature constituents of the system the stability of the incongruous compound is apparently increased.

Thus, the general structure of the diagram of our system is closely connected with the melting points of the components and of the compounds formed from them.

As is shown by the tetrahedral face systems and their binary constituents, in the majority of cases solid solutions are present in the solid phases of our system, and not the pure components; these solid solutions are formed by two, three, and in some cases it must be supposed, by all four components.

In view of the fact that the objective of the present work was to obtain a complete diagram of the liquidus, it is natural that we do not have any special figures with regard to the question of composition and changes in the solid phase, which consists in the overwhelming majority of cases of a complicated solution. Therefore we have conditionally accepted as our solid phase, with regard to the volumes of crystallization described as parts of our system, those components which are present in predominating amounts in the given solid solutions.

All the components of the system Tl, Ag, K, Na ||$NO_3$ have polymorphous modifications. In the study of the quaternary sections lines were shown which corresponded to the polymorphous transformations.

In the diagram of our quaternary system generalizing all the experimental results of the quaternary sections and tetrahedral face systems, we have surfaces of polymorphous transformations. The volumes of crystallization of $TlNO_3$, $AgNO_3$, $KNO_3$ are divided into two parts, corresponding to the polymorphous modifications, with surfaces of polymorphous transformation ($TlNO_3$ 142°, $AgNO_3$ 159°, $KNO_3$ 129°). In addition, near the corners $KNO_3$ and $NaNO_3$, there are surfaces of polymorphous transformation of the secondary variety ($KNO_3$ 315° and $NaNO_3$ 275°). Surfaces of polymorphous transformation are shown in the wire model of the diagram of our system, and can be seen in Figs. 26 and 27. Thus, the property of polymorphism somewhat complicates our diagram, without intro-

ducing any change of a fundamental character.

In conclusion, we must observe that the diagram of the melting points of the quaternary system studied, $TlNO_3$ — $AgNO_3$ — $KNO_3$ — $NaNO_3$, has a fairly complicated and peculiar character.

As a result of the absence in the literature of any description of examples of quaternary systems of melting points with a common ion, it is impossible to make any comparisons. It is difficult also to speak of any classifying types of chemical diagrams of quaternary systems. However, our chemical diagram permits us to make an attempt to single out indices of classification, and it is possible in a limited way to determine that the chief point of departure for this purpose is the character of the tetrahedral face systems. Therefore, starting from the character of the face systems, it is possible to foresee the following basic types of quaternary systems of melting points (quaternary systems with a common ion).

I. Systems without chemical interaction of the components (diagrams without chemical change).

1. The type of chemical diagram in which the tetrahedral face systems have a single ternary eutectic, and chemical compounds as well as solid solutions are absent. The diagram of the system has one quaternary eutectic. This type of diagram has been described by N. C. Kurnakov [4].

2. The type of chemical diagram in which the face systems have solid solutions, and there are no chemical compounds.

3. The type of chemical diagram where in the face systems there is observed the phenomenon of mutual insolubility or limited solubility of the components in liquid condition (separation into layers).

II. Systems in which there is chemical interaction of the components (diagrams with chemical change).

4. The type of chemical diagram where the face systems have binary chemical compounds. The chemical compounds give rise to additional quaternary points, and depending on the nature of the compounds, whether congruent or incongruent, the quaternary points will have a eutectic or peritectic character. Solid solutions are not present.

5. The type of chemical diagram where there is observed in the face systems the presence of a ternary compound, or ternary compounds. The diagram must have several quaternary points of a transitional or eutectic character. Solid solutions are absent.

6. The type of chemical diagram with a quaternary chemical compound. In the simplest case the diagram of this type must have four quaternary points.

There is reason to suppose that in addition to these 6 fundamental types of diagrams, in practice there would most often be found different combinations of types, for example, the combination of solid solutions with various chemical compounds, the presence of the phenomenon of separation into layers in the systems with chemical compounds, and so on.

## SUMMARY

1. Using a visual thermal method of analysis, a study has been made of the quaternary system $TlNO_3$ — $AgNO_3$ — $KNO_3$ — $NaNO_3$.

2. Our quaternary system has been represented by the following six quaternary sections:

I (90% $AgNO_3$ + 10% $TlNO_3$) — $KNO_3$ — $NaNO_3$,

II (70% $AgNO_3$ + 30% $TlNO_3$) — $KNO_3$ — $NaNO_3$,

III (56% $AgNO_3$ + 44% $TlNO_3$) — $KNO_3$ — $NaNO_3$,

IV (50% $AgNO_3$ + 50% $TlNO_3$) — $KNO_3$ — $NaNO_3$.

V (35% $AgNO_3$ + 65% $TlNO_3$) — $KNO_3$ — $NaNO_3$.

VI (20% $AgNO_3$ + 80% $TlNO_3$) — $KNO_3$ — $NaNO_3$.

Every quaternary section was represented as a ternary system with regard to the polythermal diagram of melting points (triangular isotherm).

3. Figures in the literature referring to the system studied, Tl, Ag, K, Na || $NO_3$, and in addition the experimental data of the six quaternary sections were summarized in the form of a general liquidus diagram of the quaternary system $TlNO_3$ — $AgNO_3$ — $KNO_3$ — $NaNO_3$.

In the diagram, the following 7 volumes of crystallization are marked: 1) the volume for $TlNO_3$, 2) the volume for $AgNO_3$, 3) the volume for $KNO_3$, 4) the volume for $NaNO_3$, 5) the volume for the compound $TlNO_3 \cdot AgNO_3$, 6) the volume of the compound $AgNO_3 \cdot KNO_3$, 7) the volume of continuous solid solutions of $KNO_3$ + $NaNO_3$. The largest volumes of crystallization belong to the highest melting salts, $KNO_3$ and $NaNO_3$. The diagram has four quaternary points, of which two are transitional, one intersectional, and one eutectic. The quaternary eutectic point corresponds to a temperature of 76° and a composition of 45.8% $TlNO_3$, 52% $AgNO_3$, 0.5% $KNO_3$ and 1.7% $NaNO_3$.

Melts in the volume of crystallization of the incongruous compound $AgNO_3 \cdot KNO_3$, as was noted also in the ternary system $TlNO_3$ — $AgNO_3$ — $KNO_3$, show great viscosity before crystallization.

4. The diagram of our system, Tl, Ag, K, Na || $NO_3$, demonstrates the influence of the melting points of the components and the compounds formed from them upon the character of the chemical diagram.

5. A classification of quaternary systems with a common ion is proposed, starting from the character of the tetrahedral face systems. The following six basic types of diagrams are foreseen:

I. Systems without chemical interaction of the components (diagrams without chemical action).

1. The type of chemical diagram in which the face systems have a single ternary eutectic, and there are neither chemical compounds nor solid solutions.

   The diagram of the system has a single quaternary eutectic.

2. The type of chemical diagram in which the face systems have solid solutions, but chemical compounds are absent.

3. The type of chemical diagram in which the phenomenon of separation of liquid layers is observed in the face systems.

II. Systems in which chemical interaction of the components is observed (diagrams with chemical action).

4. The type of chemical diagram where the face systems have binary chemical compounds, and solid solutions are absent. The chemical compounds require additional quaternary points, and depending on the kind of compounds, whether congruent or incongruent, the quaternary points will be of a transitional or eutectic character.

5. The type of chemical diagram in which the presence of a ternary compound, or ternary compounds, is observed in the face system. The diagram must have several quaternary points of a transitional or eutectic character. Solid solutions are absent.

6. The type of chemical diagram with a quaternary chemical compound.
   In the simplest case, the diagram of this type must have four quaternary points.
   Confining ourselves to the proposed classification, we see that the diagram of our system must correspond to the combined type (combination of types 2 and 4).

7. The diagram of our system $TlNO_3$ — $AgNO_3$ — $KNO_3$ — $NaNO_3$, as an example of a

genuine chemical diagram of a quaternary salt system with a common ion, has great interest.

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In conclusion, I consider it my pleasant duty to express my sincere thanks and acknowledgement to my father, Professor Alexander Pavlovich Palkin, for his guidance, counsel, and aid in the completion of my present work.

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# PHYSICO-CHEMICAL ANALYSIS OF THE SYSTEM: ACETIC ACID–NITRIC ACID

## IV. HEAT OF MIXING

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In our three previous papers, we have given the results of our investigation of the system under consideration with regard to the six physico-chemical properties: melting point, viscosity, surface tension, refraction, electrical conductivity, and density [1].

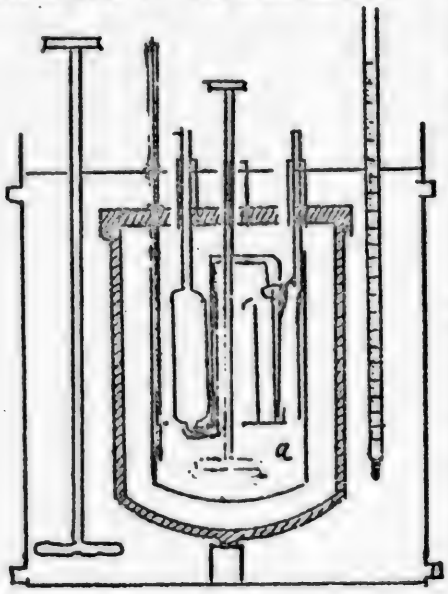
In the present article, we present the results of our investigation on the heat of mixing of this system.

It is known that the measurement of the heat of mixing of a system, and its dependence upon the composition of the mixture, can serve as a fairly decisive means of determining the chemical relation between the components of the system [2]. In view of the fact that the results of our preceding investigations on the physicochemical properties named above differ from the results of Pichtet [3], with regard to both the composition and the stability of the chemical compound formed in the system, it was of interest to investigate the system in addition from the point of view of heat of mixing, in order to obtain sufficient data for a final decision.

The chemically pure components of our system, $HNO_3$ and $CH_3COOH$, were obtained by the method described in our previous work [1].

Measurement of the heat of mixing of our system was carried out in a calorimeter with an isothermic shield.

In principal, the scheme of this calorimeter is presented in Fig. 1. The calorimetric vessel proper (a) was separated by an air space from the protecting shield.




Into this vessel, made of brass, the same quantity of water (160 g.) was poured during every measurement. In addition to a mixer and a thermometer it was fitted with a small glass reaction chamber.

The mixing of the components in the reaction chamber (after the attainment of temperature equilibrium in the initial period) was accomplished by means of a small pear-shaped convertor, joined to the right side of the chamber by rubber tubing. The liquid was poured from one chamber into the other and then, by means of careful suction, drawn back. In the course of the main period, this process of mixing was carried out 2 or 3 times.

As a check on the completeness of mixing, this same process was also repeated in the final period. No disturbance of the normal course of temperature was observed; this indicated that complete mixing of

the components had taken place during the two- or threefold process of pouring back and forth.

The temperatures of both the calorimetric vessel (a) and the shield were measured with Beckmann thermometers.

Temperature readings were made with the aid of a telescope. This permitted them to be made with an accuracy of $\pm 0.0001^{\circ}$.

Heat of Mixing of the System

| Expt. No. | Composition of Mixture (in Mol.% $HNO_3$) | Heat of mixing (in cal per mole of mixture) |
|---|---|---|
| 1 | 0.0 | 0.0 |
| 2 | 10.0 | 379.4 |
| 3 | 20.0 | 785.8 |
| 4 | 33.3 | 1068.0 |
| 5 | 40.0 | 1087.6 |
| 6 | 45.0 | 1147.0 |
| 7 | 50.0 | 1158.0 |
| 8 | 60.0 | 1106.0 |
| 9 | 70.0 | 923.0 |
| 10 | 80.0 | 695.9 |
| 11 | 90.0 | 361.8 |
| 12 | 100.0 | 000.0 |

The constancy of temperature in the protecting shield of the calorimeter was maintained by the addition of cold or hot water. Oscillations of temperature within it did not exceed $\pm 0.01^{\circ}$

The temperature at which the heats of mixing of all the different compositions were measured, varied within the limits of 20.0 to $20.7^{\circ}$.

The heat capacity of the calorimetric system "K" was not determined directly. It was calculated from the weights and specific heats of the constituents of the calorimetric system. The heat capacity of the experimentally obtained mixture of $HNO_3$ and $CH_3COOH$ was calculated on the basis of additivity from the figures given in the Handbook of physico-chemical and technical data for the pure components.

This method of calculation could not give rise to errors exceeding the accuracy of measurement, as the total quantity of the components which were mixed amounted to about 10ml., while the heat capacity of the mixture plus the heat capacity of the metal and other constituents of the calorimetric system, amounted to 10% of the heat capacity of the water poured into the calorimeter.

The correction for radiation was calculated according to the formula of Pfaundler and Ranier. In most cases, this correction did not exceed two percent of the magnitude of the observed increase in temperature, $\Delta t$, which varied, depending on the composition of the solution, from 0.349 to $1.144^{\circ}$.

The results of our measurement of the heat of mixing, recalculated per mole of mixture, are presented in the table.

The curve: molecular heat of mixing vs. composition of mixture, constructed from these data, is shown in Fig. 2.

In agreement with the classification of Roozeboom [2], the sort of curve for heat of mixing that we have obtained corresponds to the curve of an irrational system, i.e., a system in which chemical reaction takes place between the components, and the compound formed falls apart into its components as the temperature is raised.

The presence in the curve of a sharply defined maximum, corresponding to a composition of 50 mol % of each component, confirms our previous results, which had indicated that the formation of a 1:1 chemical compound ($HNO_3 \cdot CH_3COOH$) takes place in the system.

The absence of a singular point on the curve confirms the conclusion that the chemical compound formed decomposes on heating according to the equation

$$HNO_3 \cdot CH_3COOH \rightleftharpoons HNO_3 + CH_3COOH.$$

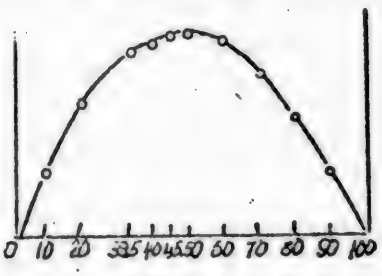



Fig. 2.

## CONCLUSIONS

1. The heat of mixing of the system: acetic acid–nitric acid, has been measured.

2. The isotherm obtained for heat of mixing vs. composition has a sharply defined maximum at 50 mol.% of the components, and consequently confirms our previous conclusions with regard to the formation in this system of a 1:1 chemical compound which decomposes into its components on heating.

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# PHYSICO-CHEMICAL ANALYSIS OF THE SYSTEM: ACETIC ACID–NITRIC ACID

## V. BOILING POINTS

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Inasmuch as the results of our previous investigations of this system[1] on seven physico-chemical properties (melting point, viscosity, density, refraction, surface tension, electrical conductivity, and heat of mixing) failed to confirm Pichtet's data [2] on the formation in the system $HNO_3$–$CH_3COOH$ of a chemical compound with the composition $HNO_3 \cdot CH_3COOH$, distilling without decomposition, it was only possible to suppose that Pichtet was dealing with an azeotropic mixture, which he had erroneously taken for a chemical compound.

In order to confirm this supposition and to clear up the question once and for all, we decided to investigate our system with regard to boiling point also.

The chemically pure acids ($HNO_3$ and $CH_3COOH$) were obtained by a method described in our previous work [2]. The determination of the boiling points of the solutions of our system was carried out in a Swientoslavski apparatus, with minor changes, introduced chiefly to protect the mixture from moisture (in view of the system's strong hygroscopic tendency) and to replace those parts of the apparatus which would be subjected to the action of the acids. Thus, for example, to protect the thermometer, an intermediate (large) reservoir was constructed inside in the shape of a deep glass "pocket", which was filled with mercury, and then had the thermometer inserted (Fig. 1). To guard against the introduction of moisture from the air, a calcium chloride tube was attached to the end of the condenser. The heating of the lower reservoir of the apparatus, containing the liquid under investigation, was carried out with the aid of a specially constructed electric oven, which permitted equal heating. To measure the temperature, we utilized an ordinary thermometer measuring to a tenth of a degree, certified. In determining the temperature, a correction was applied for the unheated mercury thread. In view of the fact that the thermometer was in a mercury pocket, and not directly in the vapor of the liquid being studied, we undertook to determine whether this might not influence the determination of the temperature. For this purpose, we conducted an experiment with distilled water; during it, it was observed that [illegible] 2 to 3 minutes after the water began to boil, the thermometer in the apparatus showed 99.9° (with P = 756 mm.). This indicated the absence of any important difference in temperature between the vapor of the boiling liquid and the reading of the thermometer inserted in the mercury pocket. After measuring the boiling points of each solution of the system, we determined

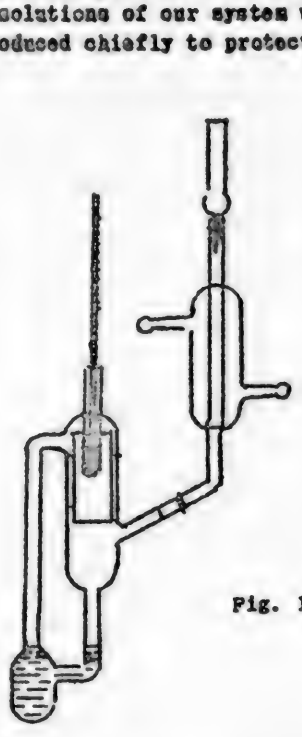
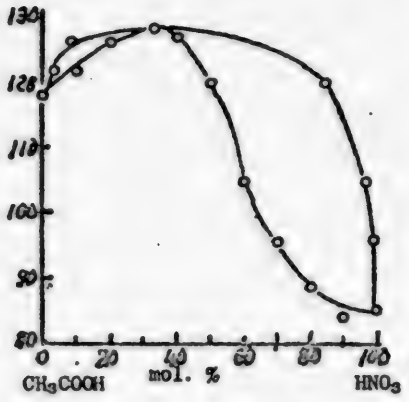


Fig. 1.

the composition of the vapor phase by collecting a small quantity (0.2–0.3 ml.) of condensate from the condenser, and measuring its refractive index by means of an Abbe refractometer.

Fig 2



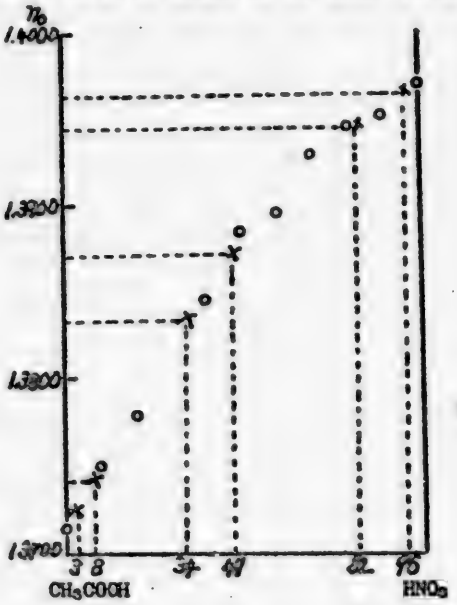




Fig. 3.

From the data obtained, we determined the composition of the vapor phase (Fig. 3) by means of the previously obtained curve showing refractive index vs. composition of the liquid phase.

In the table, we present the results of our measurements of the boiling points of solutions of the system, showing refractive indices of the liquid and vapor phases and the composition of the vapor phase.

In Fig. 2, we present the curve showing the boiling points of the system against the composition of the liquid phase, and another curve for the vapor phase.

| No. of solution | Comp. of liquid (in mol.% $HNO_3$) | B.P. at P = 756 mm (°C) | Measured index of refraction of liquid phase $n_D^{24}$ | Measured index of refraction of vapor phase $n_D^{24}$ | Comp. of vapor phase (mol.% $HNO_3$) |
|---|---|---|---|---|---|
| 1 | 0.00 | 118.1 | 1.3715 | 1.3715 | 0 |
| 2 | 10.00 | 122.1 | 1.3750 | 1.3725 | 3 |
| 3 | 20.00 | 126.5 | 1.3782 | 1.3742 | 8 |
| 4 | 33.33 | 128.6 | 1.3838 | 1.3835 | 34 |
| 5 | 40.00 | 127.3 | 1.3846 | 1.3872 | 47 |
| 6 | 50.00 | 120.3 | 1.3886 | 1.3945 | 82 |
| 7 | 60.00 | 105.0 | 1.3896 | 1.3965 | 96 |
| 8 | 70.00 | 95.7 | 1.3931 | 1.3970 | 100 |
| 9 | 80.00 | 88.6 | 1.3945 | 1.3972 | 100 |
| 10 | 90.00 | 84.0 | 1.3951 | – | 100 |
| 11 | 100.00 | 85.3 | 1.3970 | – | 100 |

## EVALUATION OF RESULTS

From Fig. 2 it is clear that our system contains an azeotropic mixture with a maximum boiling point (128.6°).

The composition of the azeotropic mixture, as is easily seen, corresponds exactly to 33.3 mol.% of nitric acid; there is no doubt, therefore, that Pichtet was dealing with an azeotropic mixture, and mistook it for a chemical compound, as this composition also corresponds to the formula $HNO_3 \cdot CH_3COOH$.

However, it is well known that the composition of azeotropic mixtures, as a rule, does not coincide with the composition of the chemical compound formed in the system. Thus, for example, the system $HNO_3$-$H_2O$ is known to contain an azeotropic mixture composed of 68 weight % nitric acid and 32% water. Upon recalculation to molecular percent, this becomes 38 mol.% $HNO_3$ and 62 mol. % $H_2O$. From the data on melting points, viscosity, and other properties [3] it is known that in this system two chemical compounds are formed ($HNO_3 \cdot H_2O$ and $HNO_3 \cdot 3H_2O$), which correspond respectively to 50 and 25 mol. % $HNO_3$.

With water, sulfuric acid gives an azeotropic mixture of the composition 98 weight % $H_2SO_4$. It is known that water and sulfuric acid give 3 chemical compounds, but not one of these compounds has a composition that coincides with the composition of the azeotropic point. Many similar examples can be adduced.

The very fact of the presence of a maximum on the boiling point curve (or a minimum of vapor pressure), that is, a departure from Raoult's Law, unconditionally confirms the fact that chemical action is taking place in the system.

As is well known, such a departure from Raoult's Law is found when the molecules of the components of the mixture are polarized, [4]. We showed previously [1] that the molecules of the components of our system are polarized. Thus, for example, according to data in the literature, the dipole moment of acetic acid equals $\mu = 0.8$ and 1.7 [5], and the dipole moment of nitric acid, according to rough calculation, equals 2.0. It is therefore comprehensible that with the presence in our system of such strongly polarized molecules, chemical action should take place between them. All our earlier investigations of this system with regard to physical chemical properties strongly confirm the existence of chemical action between the components of the system, but they all show consistently that the composition of the compound formed is not $HNO_3 \cdot 2CH_3COOH$, as Pichtet supposed, but $HNO_3 \cdot CH_3COOH$.

The chemical compound formed decomposes even at ordinary room temperature according to the scheme: $HNO_3 \cdot CH_3COOH \rightleftharpoons HNO_3 \cdot CH_3COOH$.

Upon raising the temperature, the degree of decomposition increases, and at the boiling point, the degree of thermochemical decomposition attains a very significant figure, shown also by the isotherms of viscosity and other properties.

## CONCLUSIONS

1. The boiling points of mixtures of the system acetic acid-nitric acid have been determined.

2. On the basis of the diagram obtained for composition vs. boiling point, and the curve of vapor phase composition, it is shown that the system forms an azeotropic mixture containing 33 mol. % nitric acid.

3. It is shown that Pichtet mistook an azeotropic mixture for a chemical compound.

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# THE KINETICS OF OXIDATION-REDUCTION POTENTIALS. VI*

A. L. ROTINYAN

The author, together with I. I. Appenin and V. G. Tkachenko [1], has studied the kinetics of attainment of equilibrium oxidation-reduction potentials of the system $Pt/Tl_2(SO_4)_3$, $Tl_2SO_4$; $H_2SO_4KCl_{sat.}$, $Hg_2Cl_2Hg$ with hydrogen electrodes.

In this work, we obtained kinetic curves of two types: with an S-shaped part, and with a straight-line part replacing the S. The latter has already been the subject of preliminary consideration [2].

In the present work, both types of curve are considered quantitatively from a single point of view, on the basis of the general mechanism of the process.

Upon inserting a hydrogenated platinum electrode into an oxidation-reduction system, at the very first moment, a hydrogen electrode potential is produced on the platinum.

Then the oxidation-reduction system begins to impose its own potential upon the electrode. As the potential of the system $Tl^{+++}/Tl^{+}$ lies in the region of high oxidative significance, a loss of adsorbed hydrogen must take place from the electrode until its concentration on the surface corresponds to the equilibrium oxidation-reduction potential.

In the work of A. L. Rotinyan, I. I. Appenin, and V. G. Tkachenko [1], it was assumed that under the conditions of the experiment, the reaction:

$$Tl^{+++} + 2H_{ads} \rightleftarrows Tl^{+} + 2H^{+}, \qquad (1)$$

would proceed from left to right, and that its kinetics would determine the attainment of equilibrium.

The velocity of the overall reaction (1) can be limited by the velocity of supply of trivalent thallium ions to the surface of the electrode, as well as by the velocity of the chemical reaction itself. In actual experiments, it is possible to encounter cases where the velocities of both these processes are of the same order.

The definite dependence of the speed of attainment of the potential upon the intensity of mixing of the solution testifies to the influence of the diffusion of $Tl^{+++}$ ions toward the surface upon the kinetics of the reaction. On the other hand, the activity of the electrode itself has an influence upon the kinetics of the reaction.

These and other facts [2] testify that under experimental conditions, diffusion is of the same order as reaction velocity; therefore, in the general case, we divide the question concerning the kinetics of reaction into that concerning the commensurate velocities of diffusion and the chemical reaction proper.

In considering such cases, it is convenient to utilize the method suggested by Frank-Kamenetsky [3]; however, it is necessary to keep in mind that, by its very nature, it automatically postulates homogeneity of surface.

This method has lately been utilized successfully by a number of authors (A. B. Zdanovsky, [4], M. Tovbin [5], B. V. Drozdov [6]).

It has been most completely developed by B. V. Drozdov, who integrated the differential

* Fifth paper: Proc. Acad. Sci., USSR, 46 65. (1945).

equation of the velocity which he had applied to the system he studied; this was the heterogeneous reaction involving the interchange on the surface of nickel particles.

$$Cu^{++} + Ni \longrightarrow Cu + Ni^{++}. \qquad (2)$$

In particular, B.V. Drozdov showed that on the basis of Frank-Kamenetsky's methods, it was possible to obtain an equation, entirely analogous to the empirical equation of Dintsen and Frost [7]:

$$k = \frac{1}{t} \ln \frac{1}{1 - x} - \beta \frac{x}{t} \qquad (3)$$

for the self-retarding homogeneous reaction. The coefficient $\beta$, which is less than unity, corresponds to the relative velocities of diffusion and reaction. $\beta = 1$ is the case where the kinetics are determined purely by diffusion. The other extreme case, $\beta = 0$, corresponds to purely chemical kinetics. Here x is the quantity of reacting material at time t, expressed as a fraction of unity.

It was experimentally shown that within the limits of the investigation, the velocity of reaction (1) is completely independent of the concentration of univalent thallium ions in the solution.

Consequently, in the general case of reaction (1) we may write the following expression for the velocity:

$$-\frac{dC_H}{dt} = K_1 C_H^2 C_{Tl^{+++}} - K_2 C_{H^+}^2 , \qquad (4)$$

where $C_H$ is the surface concentration of atoms of hydrogen adsorbed on the electrode at time t

$C_{Tl^{+++}}$ is the concentration of $Tl^{+++}$ on the surface of the electrode at time t;

$C_{H^+}$ is the analogous concentration of hydrogen ions;

$k_1$ and $k_2$ are the velocity constants of the direct and reverse reactions.

As the experiments showed, the electrodes with which the measurements were made, could be divided into three types, according to their activity:

First type. Slightly active electrodes, on which the kinetics curve has an S-shaped twist.

For such electrodes, the velocity of reaction is so small that for the initial period $C_H$ is of the same order as $C_{Tl^{+++}}$, and we cannot calculate the velocity of reaction independent of $C_H$.

On the other hand, no matter how little the activity of the electrode, it is natural to assume, as was done in the fifth paper [2], that the velocity of the reaction with regard to the atoms of hydrogen is not of the second, but of the first order. Then (4) can be rewritten:

$$-\frac{dC_H}{dt} = K_1 C_H C_{Tl^{+++}} - K_2 C_{H^+}^2. \qquad (5)$$

Below it will be shown that (5) holds for experiments where (4) does not hold; therefore, we shall from now on utilize equation (5) instead of (4).

Second type. The electrodes are somewhat more active. For the first period of the reaction, the inequality $C_H \gg C_{Tl^{+++}}$ holds, but later, the velocity of this part depends only on the concentration of trivalent thallium ions on the surface of the electrode; in the final period, the inverse relation holds: $C_H \ll C_{Tl^{+++}}$ and the velocity varies as $C_H$ to the first power.

Third type. Electrodes very active. In the first period, this case is distinguished from the preceding only by the greater value of the velocity constant, while in the final period the velocity of reaction depends only on $C_H$, being proportional to the concentration of adsorbed hydrogen atoms raised to the second power.

These characteristics of electrode behavior make their appearance upon reaching a

potential of +0.9 V, at which, according to Ershler's data [8], there begins the oxidation of the electrode with oxygen. Consequently, the difference in the activity of the electrodes is apparently related to the capacities of the different electrodes to be oxidized in different ways.

The kinetics curves for the electrodes of the second and third types are quantitatively included in the indicated scheme [2], and we shall therefore limit ourselves here to a review of the first case.

As after a very short interval of time the velocity of reaction must become equal to the velocity of diffusion of the trivalent thallium ions to the surface, we may write:

$$K_1 C_H C_{Tl^{+++}} - K_2 C_{H^+}^2 = \frac{D}{\lambda} (C_0 - C_{Tl^{+++}}); \qquad (6)$$

where $C_0$ is the concentration of $Tl^{+++}$ on the outer surface of the motionless layer of liquid adjoining the electrode, whose thickness is $\lambda$; D is the coefficient of diffusion of the trivalent thallium ions.

As the diffusion of $Tl^{+++}$ proceeds with a finite velocity, $C_0$ must be somewhat less than the volume concentration of trivalent thallium ions $C_{ox}$ [5].

Determining $C_{Tl^{+++}}$ by (6), we obtain:

$$C_{Tl^{+++}} = \frac{\frac{D}{\lambda} C_0 + K_2 C_{H^+}^2}{K_1 C_H + \frac{D}{\lambda}}. \qquad (7)$$

Substituting (7) into (5), we obtain:

$$-\frac{dC_H}{dt} = \frac{\frac{K_1 D C_0}{\lambda} C_H + K_1 K_2 C_{H^+}^2 + C_H}{K_1 C_H + \frac{D}{\lambda}} - K_2 C_{H^+}^2. \qquad (8)$$

For the transition from the surface concentration of hydrogen ions to the easily measured electrode potential, we shall to the first approximation consider the capacity of the double layer ($\varepsilon$) as independent of the potential.

Then from the equation:

$$-\frac{dC_H}{dt} = \frac{\varepsilon}{nF} \cdot \frac{dE}{dt}, \qquad (8a)$$

it is easy to obtain the approximate relation [2]:

$$C_H = \frac{\varepsilon}{nF} (E_p - E) = \frac{\varepsilon}{nF} \Delta E, \qquad (9)$$

which satisfactorily expresses the difference of the potentials from their equilibrium value.

Here $E_p$ is the equilibrium potential of the oxidation-reduction electrode, and E the potential at any moment which corresponds to the given concentration of hydrogen atoms adsorbed on the electrode.

Substituting (9) in (8), we obtain:

$$w = \frac{dE}{dt} = \frac{\frac{K_1 D C_0}{\lambda} \Delta E + K_1 K_2 C_{H^+}^2 \Delta E}{\frac{K_1 \varepsilon}{nF} \Delta E + \frac{D}{\lambda}} - \frac{K_2 C_{H^+}^2 nF}{\varepsilon}. \qquad (10)$$

Equations (8) and (10) may be subjected to integration; however, in connection with the indefiniteness of the value of the potential at time t = 0, it is more convenient to carry out

the experimental verification of (10) in the following manner; let us write (10) thus:

$$\frac{W}{\Delta E} + \frac{K_1 \varepsilon \lambda}{DnF} W + \frac{K_2 C_{H^+}^2 nF}{\varepsilon \Delta E} - K_1 C_0 = 0 . \qquad (11)$$

At the moment of inserting the electrode in the solution, that is, at $t = 0$, $W = 0$. Consequently, from formula (11):

$$\frac{K_2 C_{H^+}^2 nF}{\varepsilon \Delta E_{t=0}} - K_1 C_0 = 0 , \qquad (12)$$

that is, the curve must pass through the origin.

From (12) we obtain

$$C_0 = \frac{K_2}{K_1} \cdot \frac{C_{H^+}^2 nF}{\varepsilon \Delta E_{t=0}} . \qquad (13)$$

In equation (11), the term -

$$\frac{K_2 C_{H^+}^2 nF}{\varepsilon \Delta E}$$

expresses the influence of the reverse reaction.

If $K_2 \ll K_1$, then (11) is converted into the approximate equation:

$$\frac{W}{\Delta E} + \frac{K_1 \lambda \varepsilon}{DnF} W - K_1 C_0 = 0 . \qquad (14)$$

where at $t = 0$, $K_1 C_0$ can only tend toward zero, without being equal to zero, as, strictly speaking, would be expected.

Consequently, if we grant the justification of the above equation, then the experimental data plotting $\frac{W}{\Delta E}$ against W must lie on straight lines; in this way, there are obtained three sections of straight lines with different slopes, and not a single straight line for all periods of the reaction.

In Figs. 1 and 2 are given those results from the work of Rotinyan, Appenin, and Tkachenko [1] which have served for testing equation (14). On the basis of the experimental data, large scale curves of the kinetics were drawn, by means of which the value of the derivative dE/dt was graphically determined. In this way, there were obtained values for the velocity of establishment of the potential as a function of time as depicted in Figs. 3 and 4.

In Figs. 5, 6, 7, 8, and 9 are presented the results of verification of formula (14) according to the data of Figs. 1 and 2.

The straight lines of the different parts are constructed so that there is no break between them, that is, the first part includes the data up to the minimum of velocity, the second from the minimum to the maximum, and the third from the maximum of velocity to the end of the reaction. As can be seen from Fig. 5 for the first part, the data of all the curves of Fig. 1 lie along a single straight line. The angular coefficient

$$\frac{K_1 \lambda \varepsilon}{DnF} \qquad (15)$$

for the given part, is independent of the dilution, or more properly, of the concentration of trivalent thallium ions in the solution.

The independence of the angular coefficient of the curve from the concentration of $Tl^{+++}$ ions follows directly from (15), if we consider that the capacity of the double layer in the given part is not a function of the concentration. The latter may correspond to the actual case if we assume that in the first second after the introduction of the electrode into the

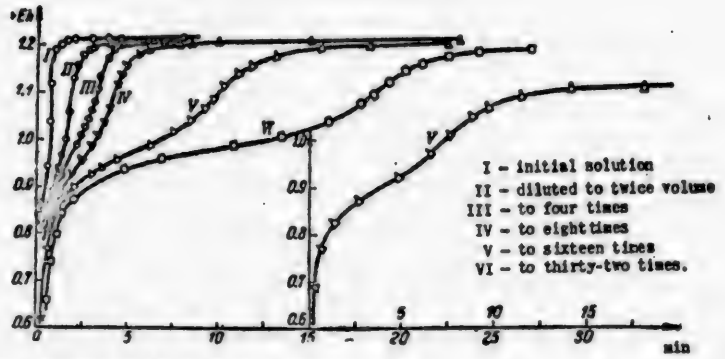
I – initial solution
II – diluted to twice volume
III – to four times
IV – to eight times
V – to sixteen times
VI – to thirty-two times.
min

Fig. 1. Influence of the dilution on the speed of attainment of equilibrium potentials.

Starting with a solution containing in mols per liter: $Tl_2(SO_4)_3$–$1 \cdot 10^{-3}$; $Tl_2SO_4$–$0.625 \cdot 10^{-4}$, $H_2SO_4$–0.174. Electrode No. 3, dimensions 25·6·0.1mm. Temp. 25°.

In the righthand corner is drawn the curve obtained with electrode No. 14, measuring 25·6·0.1mm, in a solution containing in mols per l. $Tl_2(SO_4)_3$–$0.625 \cdot 10^{-4}$, $Tl_2SO_4$–$0.312 \cdot 10^{-4}$, $H_2SO_4$–0.174 (curve from first series of experiments). Along the axis of ordinates lie the positive values of the electrode potential, in volts, on the hydrogen scale. Along the axis of abscissas the time, in minutes, from the moment of inserting the electrode into the solution.

Fig. 2. Influence of the temperature on the velocity of attainment of equilibrium potentials.

The solution contained in mols per liter $Tl_2(SO_4)_3$–$2.50 \cdot 10^{-4}$, $Tl_2SO_4$–$0.625 \cdot 10^{-4}$, $H_2SO_4$–0.174. Electrode No. 3, 25·6·0.1 mm.

Along the ordinate axis are the positive values of the electrode potential, in volts, hydrogen scale; along axis of abscissas, the time, in minutes, from moment of inserting electrode into solution.

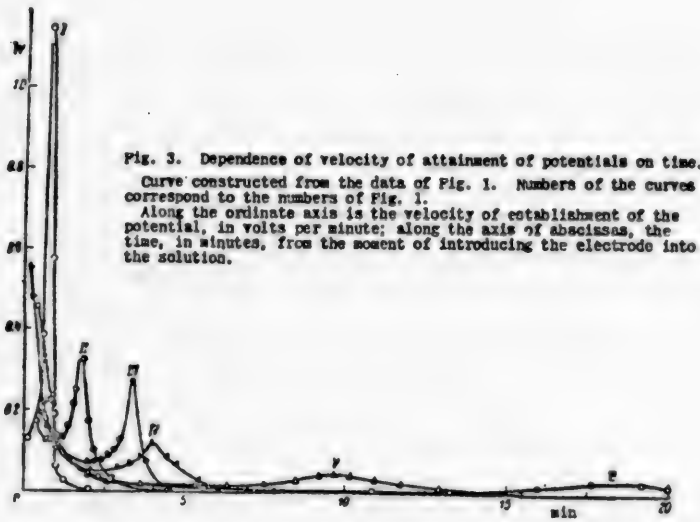


Fig. 3. Dependence of velocity of attainment of potentials on time.

Curve constructed from the data of Fig. 1. Numbers of the curves correspond to the numbers of Fig. 1.

Along the ordinate axis is the velocity of establishment of the potential, in volts per minute; along the axis of abscissas, the time, in minutes, from the moment of introducing the electrode into the solution.

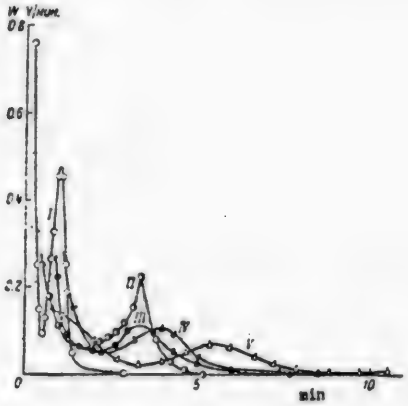


Fig. 4. Dependence of the velocity of establishment of the potentials on time.

The curves are constructed from the data of Fig. 2. The numbers of the curves correspond to the numbers of Fig. 2. Along the ordinate axis is the velocity of establishment of the potential in volts per minute; along the axis of abscissas, the time in minutes, from the moment of introducing the electrode into the solution.

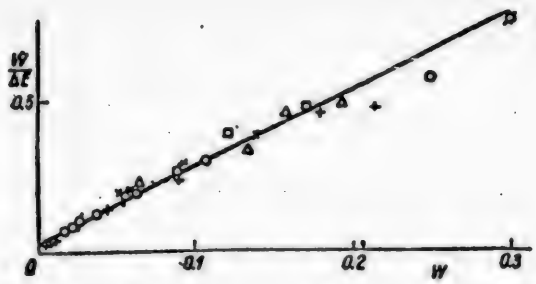


Fig. 5. Verification of equation (14) by the data of Fig. 1 (first part)

The data for curve I of Fig. 1 are not included.

□ - corresponds to curve II, Fig. 1. △ - curve III;

× - curve IV; ○ - curve V; + - curve VI.

The symbol ⊙ denotes the results for the curve drawn in the right-hand corner of Fig. 1.

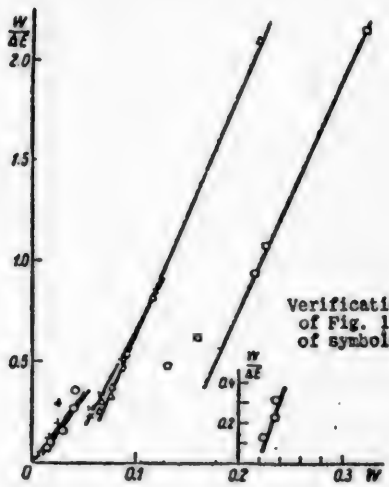


Fig. 6.

Verification of equation (14) by data of Fig. 1 (second part). For meaning of symbols, see Fig. 5.

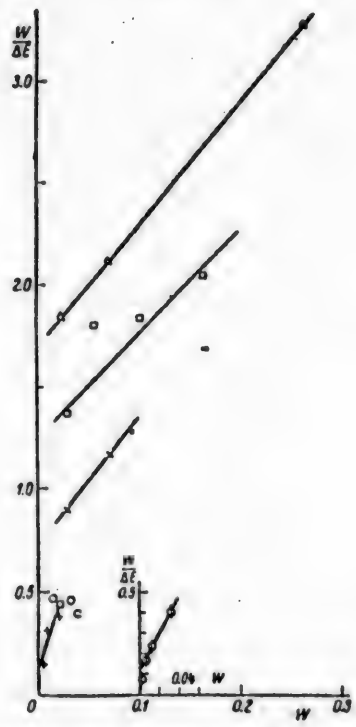


Fig. 7. Verification of equation (14) by data of Fig. 1 (third part). For meaning of symbols see Fig. 5.

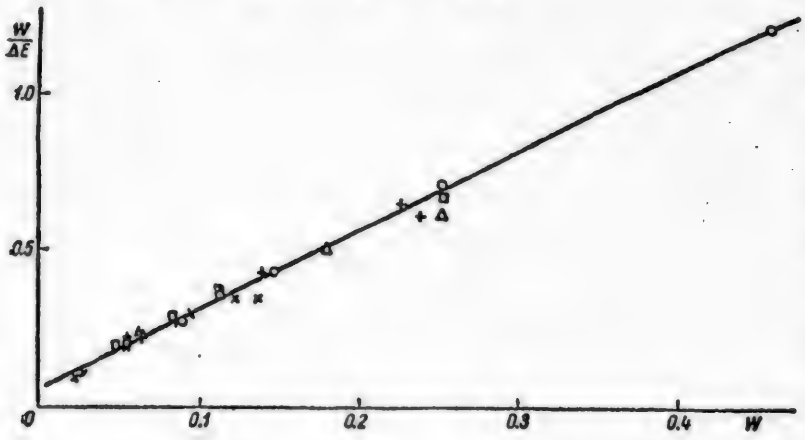


Fig. 8. Verification of equation (14) by data of Fig. 2 (first part)

○ - corresponds to Curve for temperature of 35°; △ - 25°;
+ - 17.5°; □ - 12.5°; × - 0°.

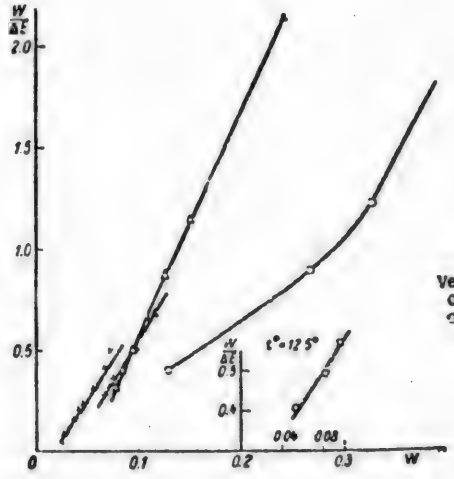


Fig. 9.

Verification of equation (14) by data of Fig. 2 (second part). For meaning of symbols, see Fig. 8.

solution, the double layer already possesses the structure of a plane condenser, while the diffused part takes time to form.

For the second part, (equation (14) is also confirmed fairly satisfactorily (Fig. 6).

Here the angular coefficient of the curve is a function of the concentration of $Tl^{+++}$ ions. Its value increases along with the increase in concentration of trivalent thallium ions, a fact which is related to the decrease in the diffusion of the double layer and the resulting increase of its capacity. In this part, as is obvious, the diffusion structure of the double layer is manifested.

Fig. 7 shows that equation (14) also represents the third part of the curves of Fig. 1. Only for curve V did the calculation fail to give a satisfactory result. The dependence of the slope upon the concentration of $Tl^{+++}$ ions in this part is not manifested with sufficient clarity. We must observe that the verification of equation (14) is justified up to the value of potentials which depart from the equilibrium value by not more than 20 mV. Consequently, the influence of the reverse reaction upon the kinetics is insignificant.

The results obtained by utilizing the data in Fig. 2 are shown in Figs. 8 and 9.

From Fig. 8 it is clear that equation (14) includes the first part of the curves, for here, as before, the points of all the curves lie well on one and the same straight line. We must suppose that the lack of dependence of the slope upon the temperature in the first part is determined by the fact that the first portion of adsorbed hydrogen atoms to react are extremely active and demand less energy of activation. In connection with this, the increase in the velocity constant with temperature is compensated by the corresponding increase of the coefficient of diffusion, and the decrease of $\lambda$.

For the second part of the curves, equation (14) is justified up to a temperature of $25^{\circ}$ (Fig. 9).

The curve obtained by plotting $W/\Delta E$ against $W$ at $35^{\circ}$ did not give a straight line, which, perhaps, is the result of a very sharp rise in the curve, and the consequent impossibility of obtaining definite values of the velocity.

The slope here increases with the rise of temperature. This, apparently, might be explained by the failure of the velocity constant to increase with the temperature to a corresponding extent. In actual fact, in this part, the less active hydrogen atoms begin to react, and consequently, the increase of the constant with rising temperature is expressed more strongly.

The data on the influence of temperature for the third part are not given graphically; from these data, we can conclude that equation (14) is justified only for the curves at 17.8 and $25^{\circ}$. At a lower temperature, the kinetics curves for this part are apparently subordinated to laws of some other kind.

It is possible to base certain calculations on the dependence of the slope upon the concentration of trivalent thallium ions and the temperature. However, we have refrained from making such calculations because we consider the experimental data of Figs. 1 and 2 insufficiently precise for this purpose. The curves obtained represent averages for 2 to 5 parallel experiments, whose reproducibility in certain cases leaves something to be desired.

On the basis of what has been presented above, we may consider that equation (14) on the whole gives a picture of the phenomenon in the given case of attainment of equilibrium oxidation-reduction potentials.

## CONCLUSIONS

We have carried out a kinetics analysis of the curves of attainment of equilibrium oxidation-reduction potentials of the system $Tl^{+++}/Tl^{+}$ on hydrogen electrodes; the experimental values were obtained by the author together with Appanin and Thachenko. We have shown that the kinetics of attainment of equilibrium potentials are conditioned by the delayed reaction which involves removal of the surplus hydrogen atoms from the surface of the electrode by the trivalent

thallium ions: $Tl^{+++} + 2H_{ads.} \rightleftarrows Tl^{+} + 2H^{+}$.

If we assume that the speed of the reaction is of the same order as the speed of diffusion of $Tl^{+++}$ ions toward the surface of the electrode, then the curve of the kinetics with an S-shaped twist can be quantitatively accounted for by the velocity equation:

$$\frac{dC_H}{dt} = K_1 C_H C_{Tl^{+++}} = K_2 C_{H^+}^2 .$$

With the introduction of several additional limiting assumptions, this equation also corresponds to the curves with straight line sections, analyzed in previous papers.

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# COMPLEX COMPOUNDS CONTAINING MAGNESIUM CHLORIDE IN AQUEOUS SOLUTION

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The question concerning the condition of magnesium chloride and the chlorides of other metals simultaneously present in aqueous solution and in melts has been investigated by many authors, who have determined the presence of molecular compounds of various compositions.

Abramov used the melting point curves of salt pairs to determine the presence of $NaCl \cdot MgCl_2$, $NaCl \cdot 2MgCl_2$, $2NaCl \cdot MgCl_2$ and $2KCl \cdot MgCl_2$.

The method of thermal analysis was used to determine the existence of $MgCl_2 \cdot CoCl_2 \cdot 8H_2O$ and $MgCl_2 \cdot AlCl_3$.

$KCl \cdot MgCl_2$ and $NH_4MgCl_3$ were found in solutions by refractometric methods. Kostashevsky, utilizing the method of electrical conductivity, ascertained the presence of $4KCl \cdot MgCl_2$ and $4NH_4Cl \cdot MgCl_2$.

A study of the equilibrium curves of the systems $KCl-MgCl_2-H_2O$ and $NaCl-MgCl_2-H_2O$ makes it seem very probable that the molecular compounds $NaCl \cdot MgCl_2 \cdot H_2O$ and $KCl \cdot MgCl_2 \cdot H_2O$ exist. A series of molecular compounds containing magnesium chloride and the chlorides of other elements has also been obtained by the evaporation of concentrated solutions of the components.

I have utilized a volumetric method for the investigation of solutions. For the preparation of the initial solutions, chemically pure components were used. The concentration of the solutions was determined by measuring the specific gravity. The initial concentration of the components in the solutions was close to the saturation point, but at the same time, there was sufficient leeway to permit work with the mixtures, without the formation of a precipitate being observed. The experiments were carried out at a temperature of 15–20°.

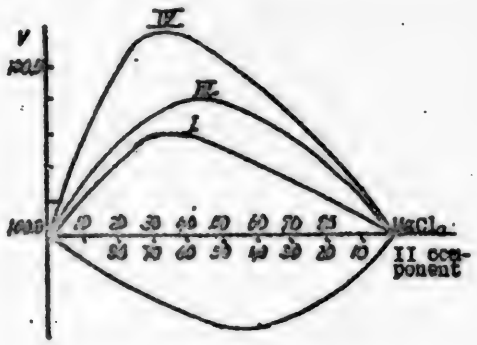
During the work, the following pairs were studied.

| | |
|---|---|
| $MgCl_2$ (4.5M.)–NaCl (5M), | $MgCl_2$ (4.5M)–$MnCl_2$ (3M), |
| $MgCl_2$ (4.5M.)–KCl (4.3M.), | $MgCl_2$ (4.5M)–$FeCl_2$ (3M.), |
| $MgCl_2$ (4.5M.)–LiCl (4.25M), | $MgCl_2$ (4.5M.)–$CoCl_2$ (1.25M.) |
| $MgCl_2$ (4.5M.)–$NH_4Cl$ (5M.), | $MgCl_2$ (4.5M.)–$NiCl_2$ (3M.), |
| $MgCl_2$ (4.5M.)–$ZnCl_2$ (5M.), | $MgCl_2$ (4.5M.)–$AlCl_3$ (1.67M), |
| $MgCl_2$ (4.5M.)–$CdCl_2$ (4.5M), | $MgCl_2$ (4.5M.)–$FeCl_3$ (5M) |
| $MgCl_2$ (4.5M.)–$CaCl_2$ (4.6M.), | $MgCl_2$ (4.5M)–$CrCl_3$ (1.12M) |
| $MgCl_2$ (4.5M.)–$SrCl_2$ (3M.), | |

With the system $MgCl_2$ (4.5 M.)–NaCl (5M), it was ascertained that upon mixing the initial solutions, there was an increase in total volume, corresponding to the formation in solution of a complex compound (Fig. 1). The character of the curve showing increase in volume of the mixture permits us to determine the presence in solution of the complex compound $Na_2MgCl_4$. An increase in volume is also observed upon mixing the pairs $MgCl_2$ (4.5 M.)–LiCl (4.25M.) and $MgCl_2$ (4.5M.)–$NH_4Cl$ (5M.) (Fig. 1).

The value of $\Delta v$ is greater for the pair $MgCl_2$(4.5M.)-LiCl(4.25M) than for $MgCl_2$(4.5M)-NaCl(5M); the maximum value of $\Delta v$ is found for the pair $MgCl_2$(4.5M)-$NH_4Cl$(5M). On the basis of the character of the curves showing increase in the volume of the mixture, we may conclude that the second and third pairs in solution also form complex compounds, $Li_2MgCl_4$ and $(NH_4)_2MgCl_4$, respectively. In studying the system $MgCl_2$(4.5M)-KCl (4.3 M), I did not observe the presence of any complex compound. All the values of $\Delta v$ were negative. Here there is a diminution in volume upon diluting the initial solutions of salts with water containing other salts in solution.

Fig. 1




Pairs:

I – $MgCl_2$(4.5 M.)-NaCl (5 M.);
II – $MgCl_2$(4.5 M.)-KCl (4.3 M.);
III – $MgCl_2$(4.5 M.)-LiCl(4.25 M);
IV – $MgCl_2$(4.5 M.)-$NH_4Cl$ (5 M.).

During a study of the pairs:

$MgCl_2$(4.5M.)-$MnCl_2$(3M.),
$MgCl_2$(4.5M.)-$FeCl_2$(3M.),
$MgCl_2$(4.5M.)-$CoCl_2$(1.25M.),
$MgCl_2$(4.5M.)-$NiCl_2$(3M.),
$MgCl_2$(4.5M.)-$CaCl_2$(4.6M),
$MgCl_2$(4.5M.)-$SrCl_2$(3M.)

no complex compounds were observed, as the value of $\Delta v$ for all the pairs was negative.

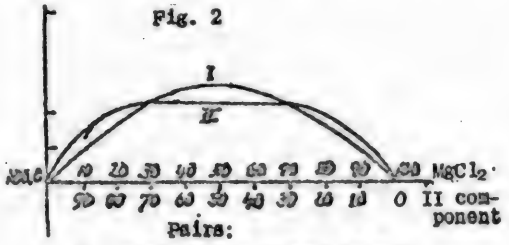
For the pairs $MgCl_2$-$ZnCl_2$ and $MgCl_2$-$CdCl_2$, there was a slight increase in the overall volume upon mixing; consequently, the formation of complex compounds takes place in solution. The position of the maximum of $\Delta v$ on curve I (Fig. 2) easily permits us to conclude that for the pair $MgCl_2$(4.5M)-$ZnCl_2$ (5M.) the complex compound $MgZnCl_4$ or $ZnMgCl_4$ is present in solution.

As is obvious from curve II, (Fig. 2), the increase in volume for the pair $MgCl_2$(4.5M.)-$CdCl_2$(4.5M) is very small.

The values of $\Delta v$ are practically identical over a comparatively great interval; apparently the solution contains at the same time complex compounds of different compositions: $2MgCl_2 \cdot CdCl_2$ ($Mg_2CdCl_6$), $MgCl_2 \cdot CdCl_2$ ($MgCdCl_4$) and $MgCl_2 \cdot 2CdCl_2$ ($MgCd_2Cl_6$).

For the first of the indicated complex compounds, the maximum of the curve corresponds to a mixture of 33.3 ml. $CdCl_2$ and 66.7 ml. $MgCl_2$, for the second, 50 ml. $MgCl_2$ and 50 ml. $CdCl_2$, and for the third, 66.7 ml. $CdCl_2$ and 33.3 ml. $MgCl_2$.

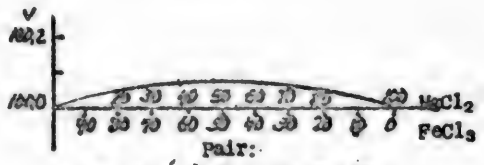
Fig. 2




Pairs:

I – $MgCl_2$(4.5 M.)-$ZnCl_2$(5 M.)
II – $MgCl_2$(4.5 M.)-$CdCl_2$(4.5 M.)

Fig. 3




Pair:

$MgCl_2$(4.5 M.)-$FeCl_3$(5 M.).

Finally, a study was made of the pairs:

$MgCl_2$(4.5M.)-$FeCl_3$(5M.),
$MgCl_2$(4.5M.)-$AlCl_3$(1.67M.),
$MgCl_2$(4.5M.)-$CrCl_3$(1.12M.)

Only in the case of the first pair was it possible to observe a positive value of $\Delta v$ (Table, Fig. 3).

In aqueous solution, $MgCl_2$ and $FeCl_3$ form complex compounds of the compositions $FeCl_3 \cdot MgCl_2$ ($MgFeCl_5$) and $2FeCl_3 \cdot 3MgCl_2$ ($Mg_3Fe_2Cl_{12}$).

As for the remaining two pairs, in every case a diminution of the overall volume was observed upon mixing the initial solutions. In aqueous solution it was impossible to detect the presence of complex compounds containing $MgCl_2$ on the one hand and aluminum or chromium chloride on the other.

As all the values of $\Delta v$ for the systems under consideration were negative, and the curve for change of volume did not on the whole permit any decision with regard to the composition of compounds existing in the solutions, I am here presenting only the most characteristic isolated values.

Concentration of solution $MgCl_2$: 4.5 M.
Concentration of solution $FeCl_3$: 5 M.
Concentration of solution $AlCl_3$: 1.67 M.
Concentration of solution $CrCl_3$: 1.12 M.

| Quantity of solution | | $\Delta v$ for the pairs | | |
|---|---|---|---|---|
| $MgCl_2$ | Second Component | $MgCl_2$-$FeCl_3$ | $MgCl_2$-$AlCl_3$ | $MgCl_2$-$CrCl_3$ |
| 0 | 100 | 0 | 0 | 0 |
| 30 | 70 | +0.06 | -1.81 | -0.35 |
| 40 | 60 | +0.07 | - | - |
| 50 | 50 | +0.08 | -1.60 | - |
| 55 | 45 | +0.08 | - | - |
| 60 | 40 | - | - | -0.88 |
| 70 | 30 | +0.06 | - | -0.80 |
| 80 | 20 | +0.04 | - | - |
| 100 | 0 | 0 | 0 | 0 |

In summarizing the experimental results, we may say that of the 15 systems considered, the presence of complex compounds in solution has been determined in 6 cases.

## CONCLUSIONS

1. The values of $\Delta v$ were determined for the increase of volume obtained by mixing the initial solutions in the systems: $MgCl_2$-NaCl; $MgCl_2$-KCl; $MgCl_2$-$NH_4Cl$; $MgCl_2$-$FeCl_2$; $MgCl_2$-$NiCl_2$; $MgCl_2$-$SrCl_2$; $MgCl_2$-$CdCl_2$; $MgCl_2$-$AlCl_3$ and $MgCl_2$-LiCl; $MgCl_2$-$MnCl_2$; $MgCl_2$-$CoCl_2$; $MgCl_2$-$CaCl_2$; $MgCl_2$-$ZnCl_2$; $MgCl_2$-$FeCl_3$; $MgCl_2$-$CrCl_3$.

2. Judging by the character of the curves for the values of $\Delta v$, the presence of the following complex compounds in solution was ascertained: $Na_2MgCl_4$, $Li_2MgCl_4$, $(NH_4)_2MgCl_4$, $MgZnCl_4$, $MgCdCl_4$, $Mg_2CdCl_6$, $Fe_2Mg_3Cl_{12}$ and $FeMgCl_5$.

3. In the systems: $MgCl_2$-KCl, $MgCl_2$-$MnCl_2$, $MgCl_2$-$FeCl_2$, $MgCl_2$-$CoCl_2$, $MgCl_2$-$NiCl_2$, $MgCl_2$-$CaCl_2$, $MgCl_2$-$SrCl_2$, $MgCl_2$-$AlCl_3$ and $MgCl_2$-$CrCl_3$, no complex compounds were detected in solution by the use of the volumetric method.

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# HYDROGENATION OF SINGLE-RING AROMATIC COMPOUNDS WITH COBALT AS CATALYST

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From the published data of A.V. Lozovoi and M.K.Dyakova [1], A.A.Alchuzhdan, A.V. Frost [2], R. Truffault [3] and M.K.Akhmedli [4], it is known that with the increase in the number of methyl groups on the benzene nucleus, the velocity of hydrogenation of single-ring aromatic hydrocarbons decreases. P. Sabatier [5] expresses the opposite opinion: he believes that toluene and xylene are hydrogenated more easily than benzene.

A.V. Lozovoi considers that the difference in the velocities of hydrogenation of single ring aromatic hydrocarbons arises, in the first place, from the formation of a chem-sorption complex of the nickel catalyst with the hydrocarbon to be hydrogenated, resulting from the free valences of the nickel atoms; and in the second place, from the different degrees of probability of the formation of such a complex for hydrocarbons with various types of double bonds and different structure.

A.V.Lozovoi does not attempt to explain why the length and configuration of alkyl groups does not influence the velocity of hydrogenation, in view of the fact that the complicated configuration of alkyl groups constitutes a more effective screen than a single methyl group (compare isoamyl benzene with toluol, p-xymene with mesitylene, etc.). The explanation of this behavior can be found basically in the multiplet theory of catalysis of A.A. Balandin[6]. The sextet principle of the multiplet theory very successfully explains the mechanism of the hydrogenation of benzene and its homologues over a nickel catalyst. M.I.Kobzev [7] considers the sextet principle not necessarily applicable to the hydrogenation of toluene. Y.N. Lapin and A.V.Frost [8] assume that in the case of palladium catalyst the active center consists of two atoms of the metal, but in the case of nickel it consists of several atoms; the dehydrogenation of cyclohexane would proceed in three stages, and at each step two atoms of hydrogen would be detached.

If this were the case, we might be expected to observe, in the first place, during the dehydrogenation of cyclohexane over metal catalysts, the intermediate compounds of cyclohexene and cyclohexadiene, whereas A.A.Balandin[6] has shown that the removal of the six atoms of hydrogen from cyclohexane takes place at a single step; in the second place, the length and configuration of the radical might actually be expected to have some influence, during the rotation of the nucleus around the doublet, on the speed of hydrogenation of single-ring aromatic hydrocarbons, whereas experimental results by the present writer and by A.V.Lozovoi and M.K. Dyakova have shown that the opposite is true. Starting from the basic postulate of the polarization theory of catalysis, we shall confirm the fact that the sextet principle of the multiplet theory offers the only correct explanation of the theory of hydrogenation of single-ring aromatic hydrocarbons. As can be seen from Fig. 1, benzene during hydrogenation adds all six atoms of hydrogen at one step, forming cyclohexane, which is desorbed from the surface of the sextet, with each —C=C— pair of the nucleus being hydrogenated by means of the active hydrogen of two atoms of the metal sextet.

Fig. 1

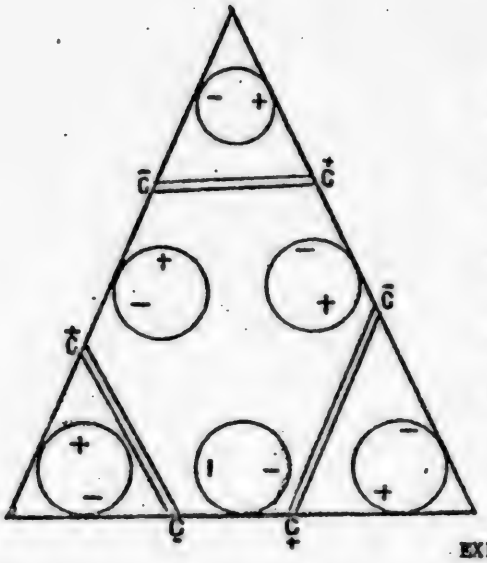
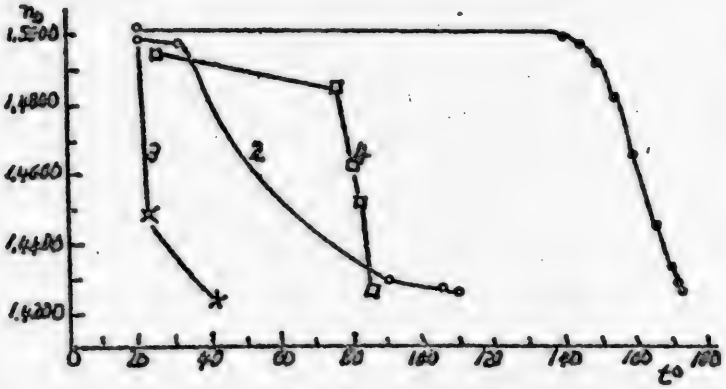


Fig. 2. Hydrogenation of Benzene over Catalysts.

I – Co; 2 – asbestos + Co; 3 – Chromium oxide + Co; 4 – aluminum oxide + Co.




## EXPERIMENTAL

In the present work, a study was made of the deep hydrogenation of benzene, toluene, and xylene, over various cobalt catalysts produced from the formate.

TABLE I

| Material from which catalyst was prepared | Composition of catalyst | Percent (by weight) | |
|---|---|---|---|
| | | Carrier | Metal |
| 1. $Co(COOH)_2$ | Co | 0 | 100 |
| 2. Asbestos + $Co(COOH)_2$ | Asbestos + Co | 38.46 | 61.54 |
| 3. Aluminum oxide + $Co(COOH)_2$ | $Al_2O_3$ + Co | 21.25 | 68.75 |
| 4. Chromium oxide + $Co(COOH)_2$ | $Cr_2O_3$ + Co | 38.46 | 61.54 |
| 5. Asbestos | Asbestos | 100 | 0 |
| 6. Aluminum oxide | $Al_2O_3$ | 100 | 0 |
| 7. Chromium oxide | $Cr_2O_3$ | 100 | 0 |

The method of preparation of these catalysts, and the manner of conducting experiments analogous to those with nickel catalysts has been reported previously [9].

According to P. Sabatier's opinion [10], as well as that of E. Maksted [11], reduced cobalt can hydrogenate benzene and its homologues at a temperature of 180°. The cobalt catalyst prepared by us from formate began to hydrogenate benzene at 140°, and at 172° converted it 100% into cyclohexane in the vapor phase, without pressure on the system of circulation. Results of the experiments are listed in Table 2, and shown graphically in Figs. 2, 3, 4, 5, 6, 7, and 8.

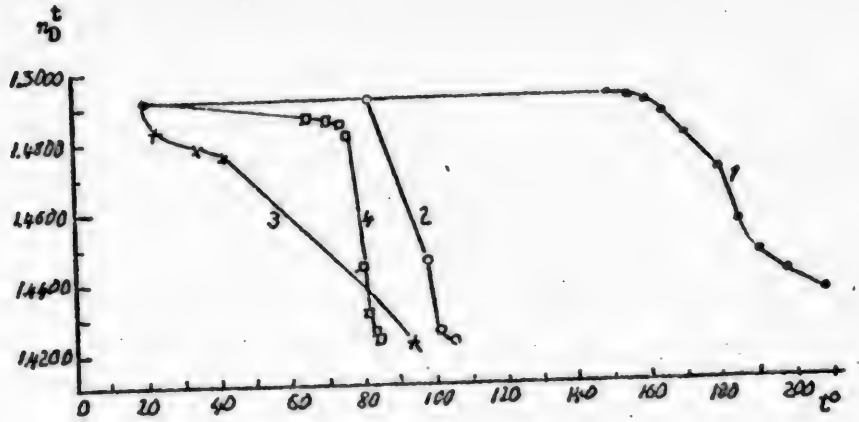
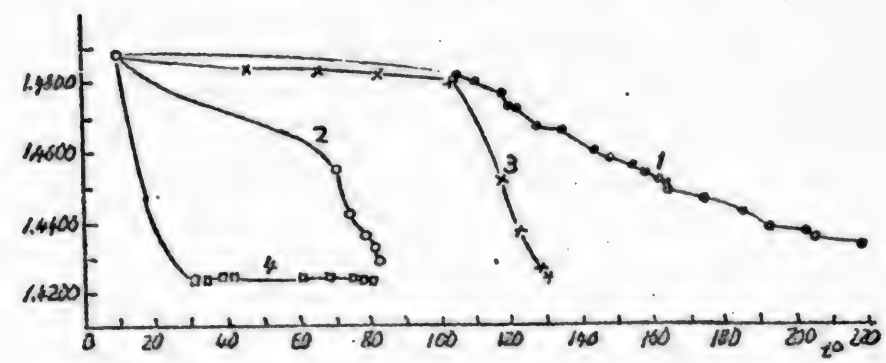



Fig. 3. Hydrogenation of toluene over catalysts

1 - Co; 2 - Asbestos + Co; 3 - Chromium oxide + Co;
4 - Aluminum oxide + Co

Fig. 4. Hydrogenation of xylene over catalysts

1 - Co; 2 - Asbestos + Co; 3 - Chromium oxide + Co;
4 - Aluminum oxide + Co.



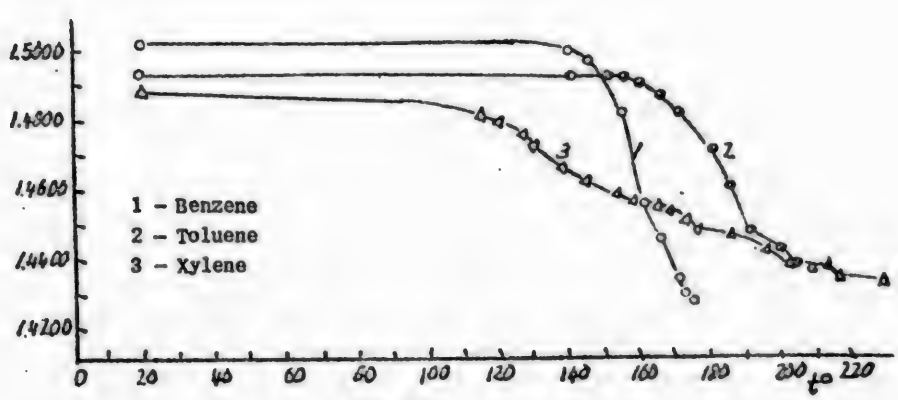




Fig. 5

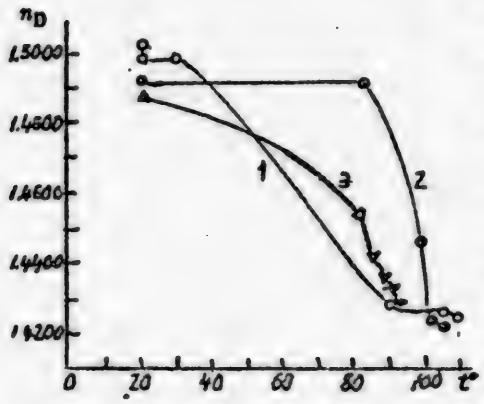



Fig. 6. Hydrogenation over asbestos + Co catalyst

1 – Benzene; 2–Toluene; 3–Xylene

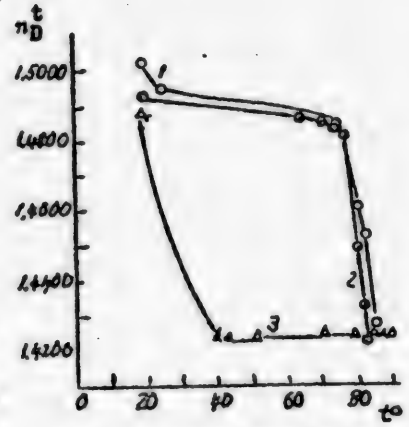



Fig. 7. Hydrogenation over aluminum oxide +Co catalyst

1 – Benzene; 2 – Toluene; 3 – Xylene.

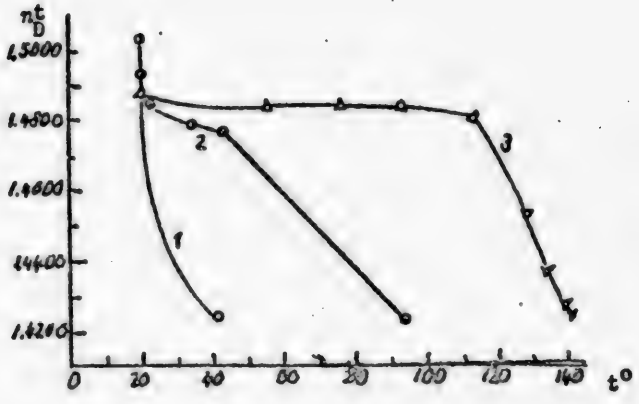



Fig. 8. Hydrogenation over chromium oxide + Co catalyst

1 – Benzene; 2 – Toluene; 3 – Xylene.

TABLE 2

| Aromatic hydrocarbon | Catalyst | Temp. of complete hydrogenation | Constants of hydrogenated material | | $MR_D$ of hydrogenate | | Percent hydrogenation |
|---|---|---|---|---|---|---|---|
| | | | $n_D^{20}$ | $d_4^{20}$ | Calc. | Found | |
| 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 |
| Benzene | Asbestos | 220 | 1.4987 | – | – | – | 0 |
| | $Al_2O_3$ | 220 | 1.4985 | – | – | – | 0 |
| | $Cr_2O_3$ | 220 | 1.4986 | – | – | – | 0 |
| | Co | 172 | 1.4276 | 0.7766 | 27.618 | 27.805 | 100 |
| | Asbestos + Co | 105 | 1.4261 | 0.7781 | 27.618 | 27.618 | 100 |
| | $Al_2O_3$ + Co | 85 | 1.4291 | 0.7817 | 27.618 | 27.53 | 100 |
| | $Cr_2O_3$ + Co | 42 | 1.4258 | 0.7781 | 27.618 | 27.58 | 100 |
| Toluene | Co | 208 | 1.4319 | 0.7781 | 30.44 | 30.84 | 100 |
| | Asbestos + Co | 100 | 1.4261 | 0.7734 | 30.44 | 30.48 | 100 |
| | $Al_2O_3$ + Co | 82 | 1.4335 | 0.7774 | 30.44 | 30.79 | 100 |
| | $Cr_2O_3$ + Co | 94 | 1.4247 | 0.7716 | 30.44 | 30.45 | 100 |
| Xylene | Co | 228 | 1.4342 | 0.7785 | 35.08 | 35.51 | 100 |
| | Asbestos + Co | 92° | 1.4313 | 0.776 | 35.08 | 35.12 | 100 |
| | $Al_2O_3$ + Co | 41° | 1.4280 | 0.7786 | 35.08 | 35.01 | 100 |
| | $Cr_2O_3$ + Co | 139 | 1.4300 | 0.7798 | 35.08 | 35.10 | 100 |

## CONCLUSIONS

From the data of Table 2 and the hydrogenation curves, the following are obvious:

1. Asbestos, aluminum oxide, and chromium oxide are not active catalysts for the hydrogenation of benzene at a temperature of 220°.

2. The degree of activity of the pure cobalt is lower than that of the mixed catalysts: asbestos + Co, $Al_2O_3$ + Co and $Cr_2O_3$ + Co (Compare Figs. 2, 3, 4).

3. The high activity of the mixed catalysts is not a property of any of the ingredients by itself, but is a joint activity of all the components of the mixed catalyst.

4. The most active catalysts for the hydrogenation of benzene and toluene are $Cr_2O_3$ + Co and $Al_2O_3$ + Co.

The most active contact surface for the hydrogenation of xylene appears to be $Al_2O_3$ + Co.

5. The hydrogenation of the compounds used (toluene, xylene) becomes more and more difficult as the number of methyl groups attached to the benzene nucleus is increased, and the speed of reaction falls in the order:

benzene > toluene > xylene

which corresponds completely to the postulate of the multiplet theory of catalysis. (Fig. 5, 8).

6. As the hydrogenation curves show, benzene reaches a maximum with greater speed than toluene and xylene, in all cases.

7. The hydrogenation of single-ring aromatic hydrocarbons to the corresponding completely hydrogenated ring hydrocarbons takes place at a single step, each $-\overline{C}=\overline{C}-$ group of the nucleus being hydrogenated by means of the active hydrogen of two metal atoms of the sextet.

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# OXIDATIVE AND OXIDATIVE-HYDROLYTIC TRANSFORMATIONS OF ORGANIC MOLECULES.

## VI. STUDY OF THE MECHANISM OF THE S. HOOKER REACTION

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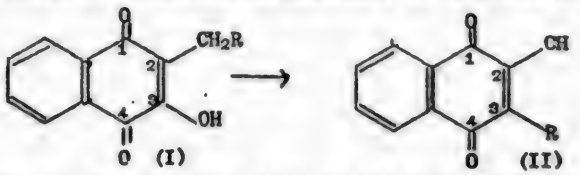
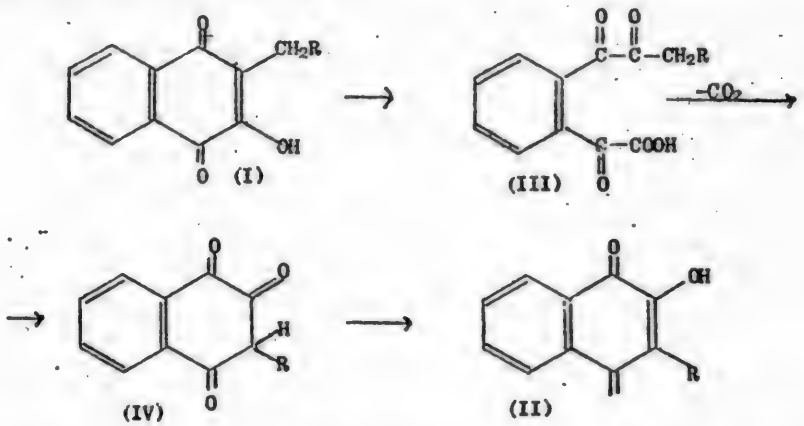
In 1936 S. Hooker reported a singular reaction [1,2]. He established the fact that hydroxynaphthoquinones of type (I) can be transformed into hydroxynaphthoquinones of type (II) when oxidized by potassium permanganate in alkaline solution:



(I) (II)

The singularity of this reaction lies in the fact that here we not only have the shortening of a side chain by one methylene group, but the simultaneous shift of the substituents at the 2 and 3 carbon atoms of the quinone ring. The latter fact was thoroughly confirmed by L. Fieser [3], using as an example a hydroxynaphthoquinone that contains the substituent (a halogen) in the aromatic ring, since only in this case could the shift of the substituents in the quinone ring be demonstrated experimentally.

Holding that this type of transformation ought to involve the opening of the quinone ring with its subsequent reclosing, in one of his papers S. Hooker advanced the following mechanism of the reaction discovered by him:



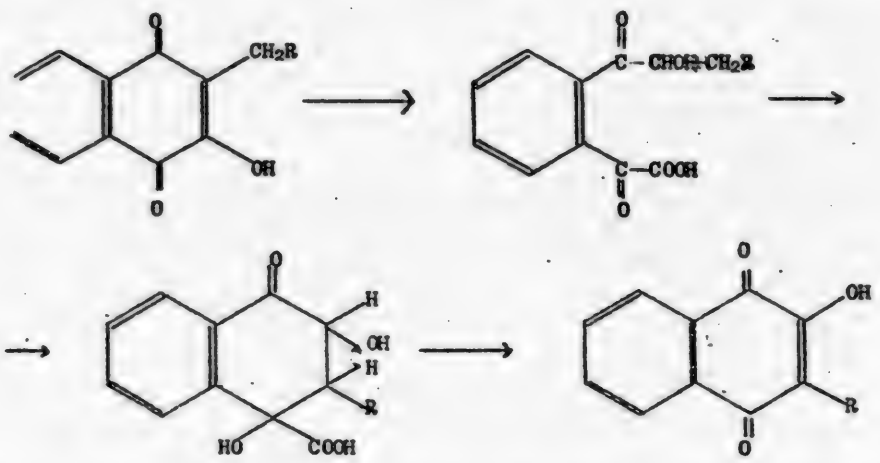
(I) (III) (IV) (II)

He noted that when an alkaline solution of a hydroxynaphthoquinone of type (I) is oxidized by potassium permanganate, the solution is first completely decolorized, only later gradually

turning red, owing to the formation of the red alkaline salt of a hydroxynaphthoquinone of type (II). If a colorless alkaline solution of this sort is acidulated before the secondary reddening of the solution sets in, the process may be interrupted. S. Hooker presupposed the presence in such a colorless acid solution of an intermediate compound (IV), whose isomerization to the terminal hydroxynaphthoquinone (II) could take place, he held, only in an alkaline medium. In this connection he believed that at the instant of the acidulation of the colorless solution it no longer contained any acid (III) that could convert into compound (IV) at that time. However, the endeavors of S. Hooker to isolate any intermediate substance met with no success, and thus the diagram suggested by him remained without experimental confirmation.

L. Feiser, who also endeavored to clear up the mechanism of these transformations, was likewise unable to isolate any intermediate compound whatsoever [3]. He did obtain one bit of circumstantial evidence, to be sure, that this reaction is accompanied by the opening of the quinone ring. He took 2-isopropyl-3-hydroxy-1,4-naphthoquinone, the oxidative cleavage of whose quinone ring ought to yield an intermediate acid of type (III), which could not be converted into the terminal hydroxynaphthoquinone of type (II) because of the absence of a methylene group alongside the carbonyl group. That is precisely why L. Fieser hoped to isolate this intermediate acid (III). He was able, however, to isolate only products of the oxidative cleavage of its molecule: phthalonic and isobutyric acids; but these could not serve as direct proof of the correctness of the reaction mechanism suggested by S. Hooker.

Subsequently L. and M. Feiser [2] suggested a somewhat different mechanism for these transformations:




But this diagram likewise failed to obtain any experimental confirmation, and thus the problem of the mechanism of the S. Hooker reaction has remained unsettled up to the present time.

In connection with our investigations, dealing with the causes and methods of the oxidative-hydrolytic cleavage of quinones we were, of course, interested in the problem of the nature of the mechanism of the reaction discovered by S. Hooker. This reaction interested us for another reason: in the general plan of our research, the clarification of the nature of the secondary transformations that take place after the cleavage of the quinone ring were no less important to us. Lastly, the observations reported by us in three preceding papers [5-8] furnished certain indications of how the study of this reaction should be approached.

Initiating these investigations, we chose as the first subject 2-methyl-3-hydroxy-1,4-naphthoquinone (phthiocol) (VIII), since it was asserted in one of S. Hooker's papers that in

the oxidation of phthiocol the conversion of the intermediate compounds into the end product 2-hydroxy-1,4-naphthoquinone takes place fairly slowly.

Our reaction differed from that effected by S. Hooker in that it took place at 15–20° instead of 0–5°. At the instant the permanganate is completely reduced, the precipitate of manganese dioxide is filtered out of the solution as rapidly as possible. An excess of 10% sulfuric acid was previously placed in the Bunsen flask into which the filtrate is drawn off, in order to break off the subsequent transformation of the initial intermediate compounds as quickly as possible. The acid solution produced is extracted with ether to eliminate the unreacted phthiocol and to aid in the formation of 2-hydroxy-1,4-naphthoquinone, after which it is evaporated to dryness in vacuum, the dry residue being extracted with ether. A light-yellow, viscous oil remains behind after the ether is driven off. Further investigation indicated that this oil was the very o-pyruvil-phenyl-glyoxylic acid (VI) that was to have been expected in this case owing to the mechanism of the reaction proposed by S. Hooker, although he held that the process does not stop at that stage, but goes further, leading to compounds of type (IV) in an acid medium.

The acid (VI) prepared by us proved to be quite soluble in water. It can be isolated only after the solvent has been eliminated. It is possible that this is the very reason why neither S. Hooker nor L. Fieser was able to isolate acids of this type in the oxidation of various hydroxynaphthoquinones of the general formula (I).

The isolated substance is a non-crystallizing oil, which cannot be purified by distillation in vacuum, since it decomposes during the process. It is extremely unstable and undergoes rapid change upon storage; as a result, all investigations must be performed with the freshly prepared product. If this compound is prepared under the conditions that are described at length in the experimental section, a fairly pure substance requiring no further purification can be obtained.

To judge by the results of titration, which must be carried out in the absence of atmospheric oxygen, the isolated compound is a monocarboxylic acid. When treated with a solution of silver ammoniate, it instantaneously forms a silver mirror in the cold; when oxidized with silver oxide, it is converted to phthalic acid. The latter observation indicates that in this substance the substituents are in the ortho position to one another.

The compound prepared is easily subjected to hydrolytic cleavage—upon storage, the moist ortho-pyruvil-phenyl-glyoxylic acid begins to convert to phthalic acid rather rapidly. The latter is often formed in quantities as high as 30% within 1–2 days. It should be noted that this process does not require the presence of atmospheric oxygen, as it takes place in an atmosphere of carbon dioxide. Hydrolytic cleavage to phthalic acid also takes place when acid (VI) is heated with water for a long time.

When ortho pyruvil-phenyl-glyoxylic acid (VI) is heated with a solution of iodine in potassium iodide in the presence of an alkali, we get iodoform. This circumstance indicates the presence of the group $-CO\cdot CH_3$ or $-CH(OH)\cdot CH_3$ in the molecule. The ability to form iodoform and the titration data exclude the possibility that the structure of this compound is of type (IV).

In an endeavor to prepare various derivatives of carbonyl groups we encountered the following difficulty: this produced profound changes of the initial molecule. Thus, when the acid isolated by us was reacted with para nitrophenylhydrazine in an acetic-acid solution, we obtained an orange crystalline substance with a decomposition temperature of 208–209°, the empirical formula of which was $C_{16}H_{11}O_4N_3$, whereas the empirical formula of the para nitrophenylhydrazone of ortho pyruvil-phenyl-glyoxylic acid ought to be $C_{17}H_{13}O_6N_3$. These results justify the assumption that during this reaction there took place the oxidative decarboxylation of the initial molecule, resulting in the formation of 2-hydroxy-1,4-naphthoquinone, the para nitrophenylhydrazone of which was isolated by us. There are three possible isomers of this para nitrophenylhydrazone of this quinone. Unfortunately, not one of them is described in the literature. Even 2-hydroxy-1,4-naphthoquinone forms a different para nitrophenylhydrazone (red needles with

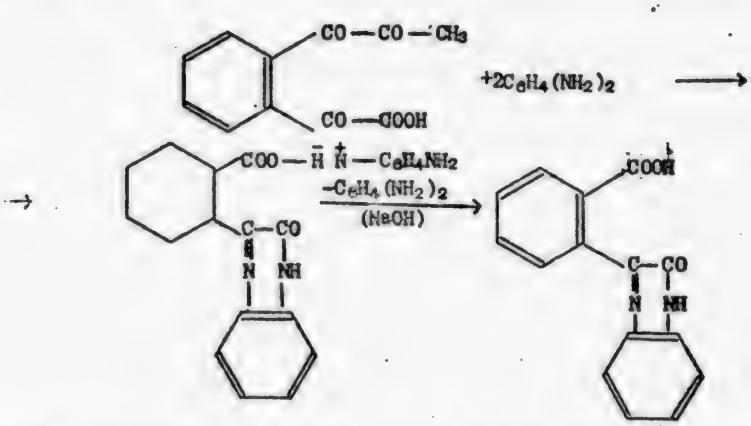
a m.p. of 173–174°) under these conditions; this is apparently an isomer of the hydrazone described above.

The reaction of ortho pyruvil-phenyl-glyoxylic acid with ortho phenylene diamine is likewise rather complicated. It was found that when this reaction is carried out in a water-alcohol solution, with heating, carbon dioxide is partially split off and two substances are formed: bright yellow needles with a decomposition temperature of 275–278° and pale yellow square flakes that decompose at 209–210°.

The first compound has the empirical formula $C_{28}H_{14}O_3N_2$. In view of the tendency of ortho pyruvil-phenyl-glyoxylic acid to close the ring (cf. below), of the formation of carbon dioxide during the reaction, and of the empirical formula given above, we are justified in assuming that the formation of this quinoxaline derivative involves not only the decarboxylation and cyclization of the initial molecule, but also the bicyclic compound formed by subsequent autocondensation. It should be emphasized that this substance can serve to identify quite minute quantities of ortho pyruvil-phenyl-glyoxylic acid, since it possesses rather characteristic properties together with extremely minute solubility in most organic solvents.

The second compound, which decomposes at 209–210°, is usually obtained only when a considerable excess of ortho phenylene diamine is used for the reaction. According to the analytical data, its empirical formula is $C_{22}H_{18}O_3N_4$; it can be titrated with alkali, and, according to the titration results, it possesses a molecular weight that corresponds to this formula. When heated in vacuum or acted upon by an excess of an aqueous solution of an alkali, this substance decomposed, forming a molecule of ortho phenylene diamine and an acid with a melting point of 240°. The latter compound had the empirical formula $C_{15}H_{10}O_3N_2$, while the titration results indicated that it was a monocarboxylic acid. It was found that this acid was the corresponding quinoxaline derivative of phthalic acid, while the substance that decomposed at 209–210° was the ortho phenylene diamine salt of this quinoxaline derivative.

The transformations described above might be represented by this diagram:

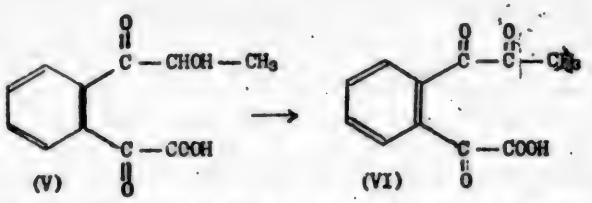



Two reactions are decisive for the proof of the structure of the ortho pyruvil-phenyl-glyoxylic acid (VI) isolated by us:

1) Its formation from ortholactyl-phenyl-glyoxylic acid when the latter is oxidized with potassium permanganate;

2) Its conversion into 2-hydroxy-1,4-naphthoquinone in an aqueous alkaline solution.

Let us dwell upon the first reaction to begin with. Ortho lactyl-phenyl-glyoxylic acid (V) was described by us in our preceding paper [6]. There is no doubt as to its structure. Hence, the fact of its oxidation to ortho pyruvil-phenyl-glyoxylic acid (VI) quite obviously indicates what the structure of the latter is:



We oxidized ortho lactyl-phenyl-glyoxylic acid with potassium permanganate in an aqueous alkaline solution, observing all the conditions under which ortho pyruvil-phenyl-glyoxylic acid is obtained from phthiocol by S. Hooker's reaction. The acid (VI) formed as the result of oxidation was identified by us as the quinoxaline derivative described above, which decomposes at 275-278°.

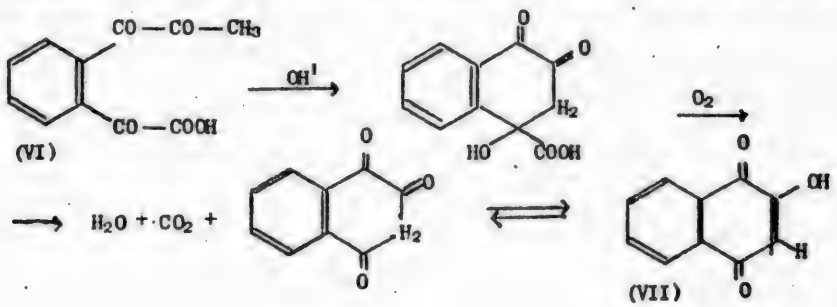
The second reaction — the conversion of ortho pyruvil-phenyl-glyoxylic acid (VI) to 2-hydroxy-1,4-naphthoquinone (VII) — takes place rapidly in an aqueous alkaline solution in the presence of atmospheric oxygen even in the cold, and extremely fast when heated. When the experiment is suitably set up (cf. the experimental section), 2 hydroxy-1,4-naphthoquinone is obtained almost quantitatively, one molecule of carbon dioxide being split off at the same time. This reaction demands the presence of atmospheric oxygen, not taking place in its absence.

It should be emphasized that the fact of the formation of 2-hydroxy-1,4-naphthoquinone from ortho pyruvil-phenyl-glyoxylic acid again demonstrates the presence of two carbonyl groups in the latter's molecule, alongside the benzene ring, as well as the presence of the $-CO-CO-CH_3$ group, which participates in the formation of the quinone ring.

Comparison of these data with the observations described above justifies the assertion that we have proved the structure of the compound isolated by us. Inasmuch as it is formed from phthiocol under the conditions of the S. Hooker reaction and is converted into 2-hydroxy-1,4-naphthoquinone under the same conditions, it is beyond doubt that it actually is the intermediate open-chain compound that is formed during the conversion of phthiocol into 2-hydroxy-1,4-naphthoquinone.

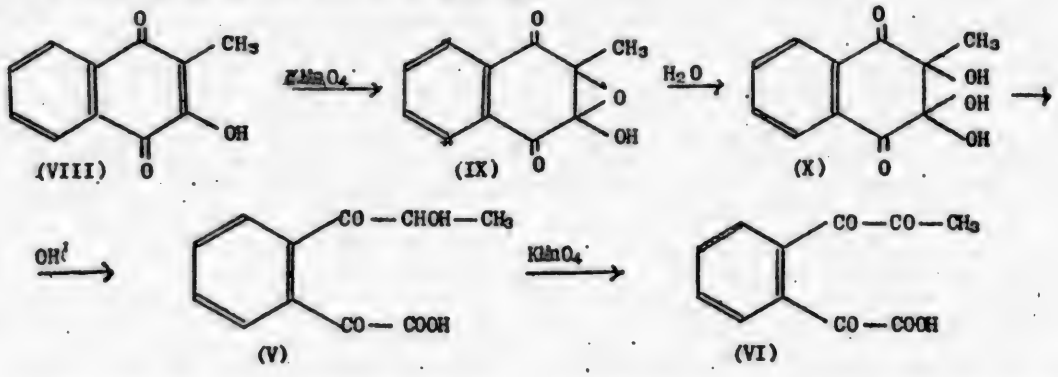
A comparison of the properties of ortho pyruvil-phenyl-glyoxylic acid (VI) with the properties of ortho lactyl-phenyl-glyoxylic acid (V) described in Communication IV [8] is especially curious. In both cases, the six-membered ring is closed upon heating with alkali in the presence of atmospheric oxygen accompanied by the liberation of one molecule of carbon dioxide and resulting in the formation of the same 2-hydroxy-1,4-naphthoquinone. In both cases this process does not take place when the oxidant is absent.

Using ortho lactyl-phenyl-glyoxylic acid as an example, we showed how the closing of the six-membered ring takes place, leading to the formation of a cyclic $\alpha$-hydroxy acid, which can undergo oxidative decarboxylation in the presence of atmospheric oxygen, forming the end product 2-hydroxy-1,4-naphthoquinone. Inasmuch as the structure of ortho pyruvil-phenyl-glyoxylic acid closely resembles that of ortho lactyl-phenyl-glyoxylic acid, and the two behave alike, it must be assumed that the liberation of carbon dioxide and the formation of 2-hydroxy-1,4-naphthoquinone take place via the following intermediate steps in this case as well.



In conclusion, we must deal with the question of how the cleavage of the quinone ring of phthiocol (VIII), resulting in the formation of ortho pyruvil-phenyl-glyoxylic acid (VI), takes place under the conditions of the S. Hooker reaction.

On the basis of the considerations set forth by us in our preceding papers, we believe that these are not purely oxidative transformations, but oxidative-hydrolytic in character. The first stage of this process, however, cannot involve the hydrolytic cleavage of the phthiocol's quinone ring. At a temperature of 15-20° this quinone is quite stable, even in more concentrated aqueous solutions of alkalis. It can be cleaved hydrolytically in alkaline solutions only at 100°, forming ortho propionyl-phenyl-glyoxylic acid, which upon further oxidation yields ortho propionyl-benzoic acid instead of ortho lactyl- or ortho pyruvil-phenyl--glyoxylic acid (cf. Paper III [8] for details). Hence, the first stage of the transformations dealt with must be the oxidation of the phthiocol molecule by potassium permanganate; the whole process may be represented by the following diagram:




At the present time we have sufficient reason to believe that the initial result of the action of oxidants upon quinones is, most often, the attachment of an oxygen atom to the position of the double bond in the quinone ring [7-14]. It follows that the oxidation of phthiocol by potassium permanganate must, to begin with, lead to the formation of the oxide (IX). It is also known that in aqueous solutions the oxides of the quinones can undergo hydration which can take place especially easily in the presence of acids or bases (cf. [8] for details). Hence, the assertion that the oxide (IX) initially formed must also exist in the hydrated form (X) under the conditions of the S. Hooker reaction will be evident enough. As for the two following steps of the process, their feasibility under these conditions was established by us experimentally. It was shown that compound (X) can undergo hydrolytic cleavage instantaneously even in the cold in the presence of as little as 1% of an aqueous alkaline solution, being converted to ortho lactyl-phenyl-glyoxylic acid (V) (see paper VIII for details). On the other hand, it was found that acid (V) in turn could be oxidized by potassium permanganate to ortho pyruvil-phenyl-glyoxylic acid under the conditions of the S. Hooker reaction (see above).

Thus there are several sufficiently weighty experimental facts that speak in favor of the diagram proposed by us for the conversion of phthiocol to ortho pyruvil-phenyl-glyoxylic acid and even to 2-hydroxy-1,4-naphthoquinone.

As for the notions developed by S. Hooker concerning the mechanism of the reaction discovered by him [4], they must be acknowledged to be correct on the basis of our data. His diagram (see above) does not, however, reflect the principal intermediate steps of either the process of cleaving the quinone ring or of its secondary formation. On the other hand, the diagram proposed subsequently by L. and M. Fieser (see above [2]) must be considered wrong, inasmuch as we have demonstrated that under the conditions of the S. Hooker reaction the acid (V) does not close the ring to form the cyclic α-hydroxy acid, but is oxidized at the instant of its formation to acid (VI), which is then converted to the terminal 2-hydroxy-1,4-naphthoquinone. The reason for this is the fact that the velocities of the conversions of acid (V)

and acid (VI) into 2-hydroxy-1,4-naphthoquinone are different. With the first of these acids the process is completed only very slowly in the cold in an alkaline solution in the presence of an oxidant, whereas it takes place very rapidly with the second acid. It should also be noted that it is usually recommended that 2 oxidative equivalents of permanganate be used to carry out the S. Hooker reaction.

## EXPERIMENTAL*

### 1. Preparation of Ortho Pyruvil-Phenyl-Glyoxylic Acid by the Oxidation of Phthiocol by Potassium Permanganate.

A solution of 2.4 g of potassium permanganate in 200 ml of a 10% aqueous solution of caustic potash is added at 15-20° with vigorous stirring to a solution of 2 g. of phthiocol on 200 ml of a 0.5% aqueous solution of caustic potash. The color of the reaction mass is observed to change rapidly from bright red through green to brown. After 2-3 minutes, when the flow on a filter paper has become nearly colorless, the reaction mass is rapidly filtered through a large Buchner funnel into a Bunsen flask, into which 230 ml of 10% sulfuric acid had previously been poured.

When the reaction is carried out rapidly, the mother liquor is transparent and yellow in color. If filtration is done too soon and the reaction of opening the phthiocol ring is not as yet complete, yellow flakes of unreacted phthiocol will settle out of the mother liquor. And if the filtration is delayed, a deposit of 2-hydroxy-1,4-naphthoquinone will precipitate out of the mother liquor. In both cases this results in a sharp decrease in the yield of ortho pyruvil--phenyl-glyoxylic acid.

The mother liquor is extracted 3 times with ether, after which the almost colorless aqueous solution is evaporated in vacuum at 5 mm and 40° (bath temperature) to a volume of about 100 ml; the excess acid is then neutralized to a pH = 4 - 4.5 by a 10% solution of soda. The solution is then evaporated to dryness in vacuum. The dry residue is extracted with ether in a Soxhlet apparatus for 3 hours. The ether solution is dried with sodium sulfate, after which the ether is driven off over a water bath. What is left is a light-yellow rather viscous oil, constituting ortho-pyruvil-phenyl-glyoxylic acid. Weight: 1.4-1.5 g. Yield: about 50%.

The substance dissolves easily in water, ether, alcohol, and glacial acetic acid. It distills over at 140° and 5 mm with decomposition and cannot be further refined by distillation. When acted upon by an ammoniacal solution of silver nitrate, a silver mirror is instantaneously formed in the cold. It turns a solution of soda or alkali red. The substance is extremely unstable in storage, decomposing rapidly and turning into phthalic acid.

Titration of this acid with a base can be done only if atmospheric oxygen is excluded, since in the presence of the latter it is very quickly converted into a bright red alkaline salt of 2-hydroxy-1,4-naphthoquinone, which makes determination of the end point difficult.

We carried out titration in a hydrogen atmosphere and in a water-alcohol solution in the presence of phenolphthalein.

0.1238 g substance: 5.92 ml 0.1 N. NaOH
$C_{10}H_7O_3 \cdot COOH$. Calculated: 5.62 ml 0.1 N. NaOH.

The somewhat large consumption of alkali is occasioned by the insufficiently precise determination of the end point, owing to the yellow color of the solution.

Determination of the methyl group by the Lieben method:

0.20 g of ortho pyruvil-phenyl-glyoxylic acid is dissolved in 5 ml of water, 0.9 g of iodine in 3 ml of a 10% aqueous solution of potassium iodide is added, and 9 ml of a 5% solution of caustic potash is poured in. The mixture is boiled for 15 minutes. The resulting iodoform

* The analytical section of our research was carried out with the assistance of E.A. Ignatyeva, to whom we are deeply indebted.

is extracted with ether, and the ether extract produced is washed with hyposulfite and then with water and dried with sodium sulfate. After the ether has been driven off, we get 0.22 g of iodoform with a m.p. of 117-118°. Yield: 61%.

2. Conversion of Ortho Pyruvil-Phenyl-Glyoxylic Acid to Phthalic Acid.

When allowed to stand in air or in an atmosphere of carbon dioxide, moist ortho pyruvil--phenyl-glyoxylic acid gradually loses its transparency, turning into white crystals of phthalic acid, which fuses with decomposition at 201-202° after having been washed with ether. One or two days later the yield of phthalic acid often attains 30%. The hydrolytic cleavage of ortho pyruvil-phenyl-glyoxylic acid to phthalic acid also takes place when its aqueous solution is heated for a long time.

Freshly prepared ortho pyruvil-phenyl-glyoxylic acid usually does not contain phthalic acid. The absence of the latter is best checked as follows: Add an alcohol solution of lead acetate to a hot alcohol solution of the sample to be tested. If phthalic acid is present; lead phthalate, which is hardly soluble in alcohol, rapidly precipitates out. The lead salt of ortho pyruvil-phenyl-glyoxylic acid is not precipitated under these conditions. The quantity of phthalic acid may be determined by the method set forth by us in paper II [15].

3. Reaction of Ortho Pyruvil-Phenyl-Glyoxylic Acid With Para Nitrophenylhydrazine.

0.9 g of the freshly prepared substance is dissolved in the minimum quantity of 80% acetic acid, and 1.5 g of para nitrophenylhydrazine likewise dissolved in the minimum quantity of 80% acetic acid, is added to this solution. The solution is allowed to stand overnight. The orange precipitate that forms is filtered out. Weight: 0.9 g. The substance is dissolved, with heat, in 18 ml of alcohol and boiled with animal charcoal; the latter is filtered out, and 12 ml of hot water added to the boiling filtrate. The precipitate that settles out after cooling fuses (decomp.) at 208-209°.

Found %: C 61.92; H 3.64; N 13.69.
$C_{16}H_{11}O_4N_3$. Calculated %: C 62.13; H 3.56; N 13.59.

4. Reaction of Ortho Pyruvil-Phenyl-Glyoxylic Acid With Ortho Phenylene Diamine.

1.5 g of the freshly prepared substance is dissolved, with heat, in 10 ml of 60% alcohol. A hot solution of 2.3 g of ortho phenylene diamine in 5 ml of water is added to the first hot solution. A precipitate settles out almost at once, with the simultaneous liberation of large amounts of gas. In a separate test it was established that the gas liberated is carbon dioxide. The reaction mass is boiled for 20 minutes, after which the hot solution is filtered. On the filter there remains a yellow precipitate, which is twice boiled with 10 ml of alcohol, filtering it while it is still hot. We get 0.7 g of bright yellow needles (Substance No. 1). Some 0.2-0.3 g of yellow flakes settle out of the alcoholic mother liquors after cooling. They can be isolated after the alcoholic solution is partially evaporated, the yield being about 0.1 g (Substance No. 2).

Substance No. 1 is insoluble in ether, alcohol, benzene, decalin, diisoamyl ether, dioxane, and a number of other organic solvents. It is insoluble in concentrated hydrochloric acid and in an aqueous solution of alkali. It is soluble solely in large quantities of hot glacial acetic acid and pyridine, from which it crystallizes out as long yellow needles. After double recrystallization from glacial acetic acid with animal charcoal added, the substance fuses with decomposition at 275-278°.

Found %: C 77.85; H 3.65; N 6.63.
$C_{26}H_{14}O_3N_2$. Calculated %: C 77.61; H 3.48; N 6.96.

Substance No. 2 is twice recrystallized from alcohol to which animal charcoal has been added. It settles out in the form of pale yellow square flakes. It fuses with decomposition at 209-210° after having been dried in vacuum at 50°; it is then allowed to solidify in a capillary, after which it fuses at 230°-240° without decomposition.

Found %: C 67.24; H 5.32; N 14.98.
$C_{21}H_{18}O_3N_4$. Calculated %: C 67.35; H 4.81; N 14.94.

The substance is titrated with alkali in an alcohol solution in the presence of phenolphthalein.

Found mol. weight 377.
$C_{21}H_{18}O_3N_4$. Calculated mol. weight 374.

Decomposition of Substance No. 2 upon Heating: The substance that decomposes at 209-210° was brought to constant weight at 40° and 5 mm. Then a weighed batch was placed in a box, and the box placed in a wide test tube that is connected to a vacuum pump. The weighed batch was heated at 130° and 5 mm until its weight was constant. The heating lasted 15 hours. The split-off ortho phenylene diamine sublimed on the cold walls of the test tube in the form of white crystals. Its m.p. was 102°.

Per cent of ortho phenylene diamine split off: 28.68.
$C_{21}H_{18}O_3N_4$. Ortho phenylene diamine content (%): 28.87.

The substance remaining after the ortho phenylene diamine had been split off and sublimed, had a m.p. of 238-240°. It was subjected to analysis without further refining.

Found %: C 67.23; H 3.94; N 10.22.
$C_{15}H_{10}O_3N_2$: Calculated %: C 67.67; H 3.75; N 10.52.

Decomposition of Substance No. 2 by Alkali: 0.5 g of the substance that decomposes at 210° was dissolved in 25 ml of a 10% aqueous solution of caustic soda. This solution was extracted several times with ether, the ether solution dried with sodium sulfate, and the ether driven off. There remained 0.1 g of ortho phenylene diamine with a m.p. of 101-102°.

After its extraction with ether, the alkaline solution was acidulated with sulfuric acid, and the slightly yellowish precipitate that settled was filtered out. M.p.: 237-238°. M.P. after recrystallization from alcohol: 240°. A test sample, mixed with the quinoxaline derivative of phthalic acid, fused at the same temperature. The compound prepared was titrated back in an alcohol solution with N/10 caustic soda in the presence of phenolphthalein.

Found mol. weight 256.
$C_{15}H_{10}O_3N_2$: Calculated mol. weight 266.

5. Action of Alkali Upon Ortho Pyruvil-Phenyl-Glyoxylic Acid.

a) Formation of 2-hydroxy-1,4-naphthoquinone. 1.0 g of the freshly prepared substance is dissolved in 100 ml of water and then placed in a three-necked flask, equipped with a dropping funnel, a reflux condenser, and a tube extending to the bottom of the flask and connected to a gas tank. 100 ml of a 1% solution of caustic potash are added. The solution immediately turns red, turning dark red upon boiling in a stream of air. After boiling for 30 minutes, the reaction mass is cooled and acidulated with 30% sulfuric acid; the yellow deposit that precipitates out is extracted with ether. The ether solution is dried with sodium sulfate, and the ether is driven off. There remains behind 0.8 g of a yellow substance with a m.p. of 185-186°. The m.p. after recrystallization from methyl alcohol is 191°. A test sample, mixed with 2-hydroxy-1,4-naphthoquinone, melts at the same temperature. From this compound we got an anilide with a m.p. of 192° and 2 hydroxy-3-nitro-1,4-naphthoquinone with a m.p. of 157°, the properties of which agreed with those reported in the literature [16,17]. The yield of 2-hydroxy-1,4-naphthoquinone is 98%.

It should be borne in mind that ortho pyruvil-phenyl-glyoxylic acid in alkaline solution and in the presence of atmospheric oxygen is converted into 2-hydroxy-1,4-naphthoquinone rather quickly and in the cold, differing markedly in this respect from ortho lactyl-phenyl-glyoxylic acid, which is easily transformed into 2-hydroxy-1,4-naphthoquinone merely upon heating.

b) Determination of the carbon dioxide formed. This determination was made with the same apparatus and under the same conditions as in the analogous experiment with ortho lactyl-phenyl-glyoxylic acid described at length in Paper IV [6] (Experiment 5b).

0.2142 g of freshly prepared ortho pyruvil-phenyl-glyoxylic acid and 50 ml of a 5% solution

of caustic potash were used for the reaction. 10.55 ml of N/10 alkaline solution used for the $CO_2$ formed. 3.22 ml of N/10 alkaline solution were used for the carbon dioxide obtained from the potash contained in the 40 ml of 5% solution of caustic potash used for the reaction. Hence, 7.33 ml of N/10 NaOH were used for the carbon dioxide formed as a result of the reaction, whereas 9.73 ml should have been used up according to computation. Yield of carbon dioxide - 75.3%.

6. Action of Alkali Upon Ortho Pyruvil-Phenyl-Glyoxylic Acid in a Hydrogen Atmosphere.

The experiment was run in a three-necked flask fitted with a reflux condenser, dropping funnel, and a tube reaching down to the bottom of the flask. The apparatus was filled with hydrogen from a Kipp generator. The hydrogen was first purified by passing it through alkaline solutions of permanganate and pyrogallol. To eliminate the last traces of carbon dioxide it was passed through an incandescent tube filled with copper and then through a Tischenko bottle filled with a 40% alkaline solution before reaching the three-necked flask. The hydrogen made its exit through the reflux condenser, then passing through a titrated alkaline solution contained in two flasks connected in series. The system terminates in a Tischenko bottle, containing an alkaline solution of pyrogallol.

0.2286 g of freshly prepared ortho pyruvil-phenyl-glyoxylic acid and 20 ml of water were placed in the flask. After the system was tested for airtightness, the air was driven out by hydrogen for 1 hour. Then 20 ml of an 11% solution of caustic soda were added from the dropping funnel, and the reaction mass was boiled for 30 minutes. This was observed to cause considerable clouding of the solution. It grew pale yellow again upon cooling, however. After having been acidulated with 30% sulfuric acid, the reaction solution was again boiled for 15 minutes in a current of hydrogen, after which the alkaline solution serving as a carbon-dioxide absorbent was titrated back with N/10 acid solution, first with phenol-phthalein and then with methyl orange.

3.84 ml of N/10 alkaline solution were used for the carbon dioxide formed. It was found in a preliminary test that 3.60 ml of N/10 NaOH was used up for the carbon dioxide formed from the potash contained in the 20 ml of 11% caustic potash solution employed in the reaction.

Thus, no carbon dioxide is formed when an alkali acts upon ortho pyruvil-phenyl-glyoxylic acid in the absence of oxygen. Nor is 2-hydroxy-1,4-naphthoquinone formed under these conditions.

7. Oxidation of Ortho-Lactyl-Phenyl-Glyoxylic Acid to Ortho Pyruvil-Phenyl Glyoxylic Acid.

A solution of 1.2 g of potassium permanganate, dissolved in 200 ml of a 10% aqueous solution of caustic potash, is added at 15-20° with vigorous stirring to 2.0 g of ortho-lactyl--phenyl-glyoxylic acid, dissolved in 200 ml of a 0.5% aqueous solution of caustic soda. Five to seven minutes later, when drops run onto filter paper are quite colorless, the reaction mass is quickly filtered through a large Buchner funnel into a Bunsen flask, into which 230 ml of 10% sulfuric acid had previously been poured. When the reaction is performed quickly, the mother liquor remains transparent and is pale yellow in color. The solution obtained is extracted three times with ether, after which the nearly colorless aqueous solution is evaporated at 40° and 5 mm to a volume of some 100 ml, and the excess acid is neutralized with soda to a pH of 4-4.5. The solution is then evaporated to dryness in vacuum. The dry residue is extracted with ether in a Soxhlet apparatus for 3 hours. The ether solution is dried with sodium sulfate, and the ether is driven off on a water bath. There remain 1.5 g of a light yellow viscous oil, constituting ortho-pyruvil-phenyl-glyoxylic acid.

The substance formed is dissolved in 5 ml of alcohol, and 2.3 g of ortho phenylene diamine dissolved in 10 ml of hot alcohol are added. A yellow precipitate is thrown down almost at once, carbon dioxide being liberated rather vigorously. The solution is heated on a water bath for 20 minutes, and the hot reaction mass is put through a filter. The orange deposit obtained is boiled three times with a small quantity of alcohol and then twice recrystallized from glacial acetic acid in the presence of animal charcoal. 0.3 g of a substance in the form of long yellow crystals are obtained, which decompose at 275-278°. A test sample, mixed with the quinoxaline derivative prepared from ortho pyruvil-phenyl-glyoxylic acid (see above, experiment 4), melts

with decomposition at the same temperature.

## CONCLUSIONS

It has been found that when phthiocol is oxidized by an alkaline solution of potassium permanganate, it undergoes a series of oxidative-hydrolytic transformations, which can be interrupted at the stage where ortho pyruvil-phenyl-glyoxylic acid is formed if certain conditions are observed. At the same time a study was made of the methods and the conditions for the conversion of ortho pyruvil-phenyl-glyoxylic acid to 2-hydroxy-1,4-naphthoquinone; it was found that this process involves the oxidative decarboxylation of the bicyclic α-hydroxy formed as an intermediate.

These investigations, using phthiocol as an example, resulted in the elucidation of the mechanism of the S. Hooker reaction.

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** (Consultants Bureau English Translation, p. 175-180. Article G-26.)

# OXIDATIVE AND OXIDATIVE-HYDROLYTIC TRANSFORMATIONS OF ORGANIC MOLECULES

## VII. HYDROLYTIC TRANSFORMATION OF A CHLOROKETONE OF THE TETRAHYDRONAPHTHALENE SERIES

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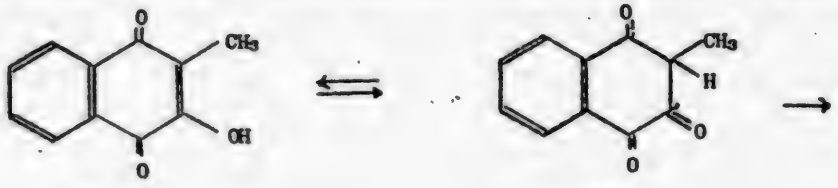
A detailed study of the nature of the hydrolytic cleavage of hydroxyquinones and the triketones that are tautomeric with them was required to settle the question of how the degree of oxidation of quinone molecules affects the tendency of their cyclic groups toward hydrolytic cleavage. In the research previously undertaken in this field it was shown [6] that the purely hydrolytic cleavage of the carbon bonds of the ring is feasible at least for 2-methyl-3-hydroxy--1,4-naphthoquinone (phthiocol) (I), which is a tautomer of the triketone (II). This was effected by boiling phthiocol with water with a pH of the solution exceeding 7, resulting in the formation of the corresponding monocyclic compound-- ortho propionyl-phenyl-glyoxylic acid (IV):



(I) (II)

(III) (IV)

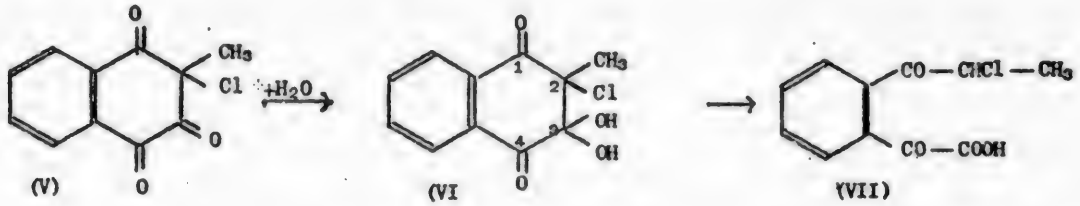
This type of cleavage may likewise occur in other hydroxy-quinones, to wit, 3-hydroxy-1,4-phenanthraquinone, which is converted, upon boiling with a dilute aqueous solution of a base, into (2-acetyl-1-naphthyl)-glyoxylic acid [6a]. Naturally, this substantial observation required further confirmation, both in the hydroxyquinone series and in the series of triketones that are tautomeric with it.

A few dihalogenated triketones of this type have been described in the literature [1,5]. All of them are easily changed in the presence of aqueous solutions of bases, undergoing a

number of transformations. To judge by the nature of the end products, it might have been thought that the first stages of these changes likewise involved hydrolytic cleavage of cyclic groups analogous to that outlined above. However, the initial reaction products of none of the compounds described has been isolated, and, hence, the initial stages of their cleavage processes remained unclear. Moreover, no study was made of the mildest conditions under which their cleavage could be effected. That is why none of these instances could serve in settling the problems that interested us.

Endeavoring to obtain results that were comparable to those described in our previous communications [a-10], we determined to investigate the conditions and the nature of the hydrolytic cleavage of a triketone that possessed a structure of type (II). For this purpose we proposed and carried out the synthesis of a chlorotriketone (V), which was subjected to detailed study.

From the experimental data on the hydrolytic cleavage of phthiocol (I) [8], as well as from the theoretical considerations set forth in communication [8], it was to have been expected that the cleavage of the cyclic groups of the chlorotriketone (V), ought to take place quite easily. Insofar as the cleavage of phthiocol was of a purely hydrolytic nature, not requiring the action of oxidants, we had to assume that in our case, too the cleavage of the ring ought to take place under the influence of solely hydrolytic agents. What is more, it had to be expected that the chlorotriketone (V) would be split much more easily than phthiocol, since the rules established previously by one of the authors (Shemyakin [11-15]) for the hydrolytic cleavage of the carbon bonds in other types of organic molecules stated that the chlorine atom in the compound (V), possessing a strong J effect, ought to facilitate this process considerably. Finally, by analogy to the reactions of the hydrolytic cleavage of phthiocol cited above, we could assume that the hydrolytic cleavage of the chlorotriketone (V) would also be preceded by its hydration, while the process itself would proceed according to the following diagram, leading to the formation of ortho (α-chloropropionyl)-phenyl-glyoxylic acid (VII) as the initial reaction product.




The experimental investigation of this problem fully confirmed our assumptions. In fact, it was found that the chlorotriketone (V) is hydrated with exceptional ease by the action of water at room temperature, being converted into compound (VI). Under the action of aqueous solutions of one weight equivalent of ammonia or caustic soda, the latter almost instantaneously undergoes hydrolytic cleavage even in the cold, being converted into ortho(α-chloropropionyl)--phenyl-glyoxylic acid (VII), whose formation we had expected. This process may also be carried out when no alkaline catalysts are present by boiling the compound (VI) with water for 30-40 minutes.

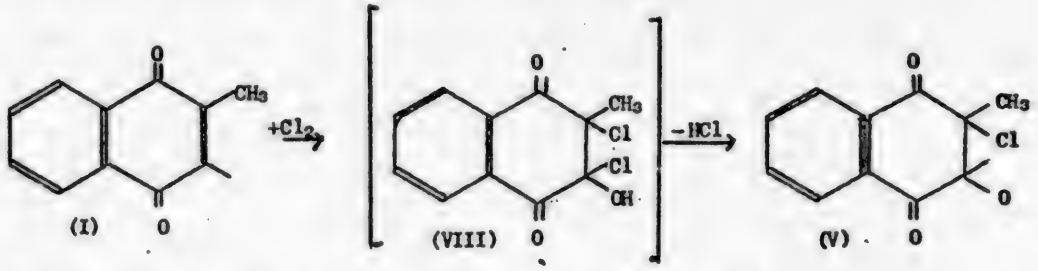
However, we noted that the hydrolytic cleavage of the bonds between the 2 and 3 carbon atoms of the ring in compound (VI) is accompanied by still another reaction, viz.: the partial substitution of a hydroxyl group for the chlorine atom, which takes place even before the cleavage of the cyclic groups. Depending on the conditions, this reaction may take place more or less completely, leading ultimately to the formation of ortho lactyl-phenyl-glyoxylic acid (IX) in addition to the acid (VII). This problem is the special subject of the following paper [16].

As we expected, owing to the auxiliary influence of the chlorine atom, compound (V) or, more precisely (VI), was found to undergo hydrolytic cleavage much more easily than is the case with compound (I) $\rightleftharpoons$ (II) or, more precisely, (III). While in the former case brief boiling of the substance with water or the action of dilute aqueous solutions of bases at 20° for a few

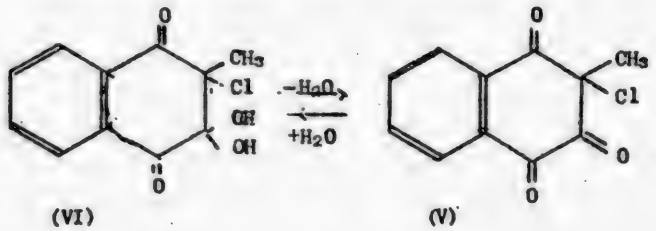
seconds suffices for the process to be carried out practically to its end, in the latter case the substance remains unaffected even after boiling with water for several hours or the prolonged action of a considerable excess of a 10% solution of caustic soda at room temperature. As was mentioned above, compound (I) $\rightleftharpoons$ (II) can undergo hydrolytic cleavage only if it is boiled for a long time in a water solution with a pH in excess of 7, i.e., under conditions that are much more rigorous than are needed in our case. Thus, our expectations were fully borne out in this respect as well.

The chlorotriketone (V) has not been described in the literature. Nor is there any mention of the general method for the synthesis of this type of compound; we were therefore compelled to find a way of preparing this chlorotriketone, and while effecting its synthesis, to indicate the structure of the substance prepared, which involved a detailed study of its properties and transformations. Finally, the compounds prepared as the result of the hydrolytic cleavage of the hydrated chlorotriketone (VI) in turn required detailed study, since none of these was known previously. The results of these investigations are set forth in detail below as well as in the experimental section.

It seemed to us that the most suitable initial product for preparing the chlorotriketone (V) might be the easily available phthiocol (I). It was known from previous work, principally by T. Zincke [1-5, 17-59, 66], that halogen atoms are easily attached to the quinones at the double bond of the quinone ring; it could therefore be assumed that an analogous reaction would take place with phthiocol. The chlorination product (VIII) formed in this case, however, would have to split off hydrogen chloride at the very instant of its formation, being thereby transformed into the chlorotriketone (V) that we desired. And indeed it was found that the chlorination of phthiocol by gaseous chlorine at 20° in a medium of anhydrous carbon tetrachloride results in the formation of the expected chlorotriketone (V):



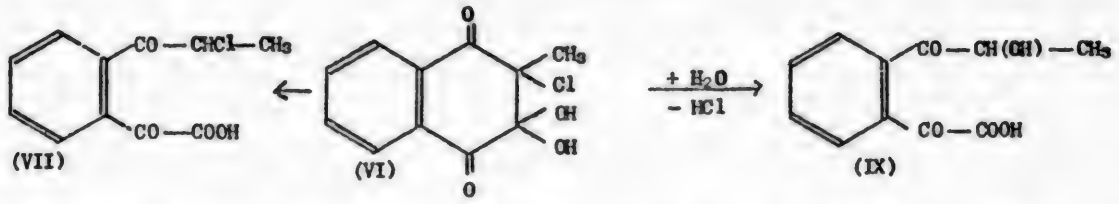

To be sure, its isolation in pure form was rather complicated in this case by the presence of hydrogen chlorine (which is being formed throughout the reaction) in the reaction mass. As a result, we later adopted the chlorination of a suspension of phthiocol in water. Under these conditions we obtain not the chlorotriketone (V) itself, but the product of its hydration (VI) in the form of a white crystalline substance with a m.p. of 102-103°. The yield of the latter is 90%. The compound does not lose a molecule of water in recrystallization from organic solvents, and hence it must be assumed that this is not water of crystallization, but chemically bound water. On the basis of these data, as well as other data, we attribute the structure expressed by Formula (VI) to the substance with a m.p. of 102-103°:



When 2-chloro-2-methyl-1,2,3,4-tetrahydronaphthalenediol-3,3-dione-1,4 (VI) is heated in vacuum at 125°, it loses water rapidly, changing into the chlorotriketone (V). The latter may be prepared in pure form after redistillation in vacuum. It is a viscous yellow liquid, which is rapidly hydrated upon standing exposed to the air, being reconverted to the crystalline compound (VI). Upon its introduction into cold water this conversion takes place almost instantaneously. When substance (V) or (VI) is heated in a benzene solution with ortho phenylene diamine, the same quinoxaline derivative, with a m.p. of 167°, is obtained.

These reactions demonstrate that the compound (VI) is a hydrated form of compound (V); hence the further confirmation of the structure of these substances was confined solely to compound (VI) as the stabler of the two.

Compound (VI), dissolved in 50% alcohol, is titrated with a N/10 solution of a base, about 1 weight equivalent of the latter being used. At the same time, however, part of the chlorine is split off (about 12-13%). More than 1 weight equivalent of the base is required when titration is effected in 50% acetone; the quantity of split-off halogen likewise increases (20-23%). Compound (VI) is fairly quickly soluble in an aqueous solution of soda in the cold and instantaneously in a solution of ammonia or caustic soda, forming a colorless solution that gradually turns red when exposed to the air. This property of compound (VI) gives rise to the impression that it is an acid. In actuality, matters are otherwise, however. As will be shown below, compound (VI) is not an acid nor does it contain a carboxyl group; but under these conditions it instantaneously undergoes hydrolytic cleavage of the ring, transforming it into two acids that are formed simultaneously viz.: ortho (α-chloropropionyl)-phenyl-glyoxylic acid (VII) and ortho lactyl-phenyl-glyoxylic acid (IX), which are titrated against a base. The first of these two acids is ordinarily obtained in a predominating quantity. They may be isolated by acidulating an alkaline solution and separated by means of their different solubilities in water and ether. Formation of the acid (IX) is linked with the replacement of the chlorine atom by a hydroxyl group. For that very reason, the presence of some chlorine ions in the solution can always be detected after the titration.




Acid (VII) is isomeric with compound (VI), but its properties are quite different. To convince ourselves still further that the substance (VI) is actually a bicyclic compound, while the acid (VII) is a derivative of benzene, we investigated a number of transformations of these two substances, which enabled us with complete certainty to ascribe to them the structure outlined above.

Compound (VI) contains three active atoms of hydrogen (as determined by the Tserevitinov-Terentyev method [64]) which agrees with the presence of 2 hydroxyl groups and a reactive methyl group in its molecule. In this compound the chlorine atom possesses marked oxidizing power: the substance quantitatively oxidizes potassium iodide to free iodine upon heating in a glacial acetic acid medium or in an alcoholic solution in the presence of hydrochloric acid. In aqueous and acetone solutions this reaction takes place easily even in the cold*. As we know [60-62], this peculiarity is most strikingly marked among the halogen derivatives in which the halogen atom is attached to the carbon atom, linked with some carbonyl or carboxyl groups or with a nitro group. For this very reason the property described may be an essential argument in favor of formula (VI). And, in fact, acid (VII) does not possess this property at all, its chlorine atom adjoining only a single carbonyl group.

The reaction between potassium iodide and an organic molecule containing a halogen atom

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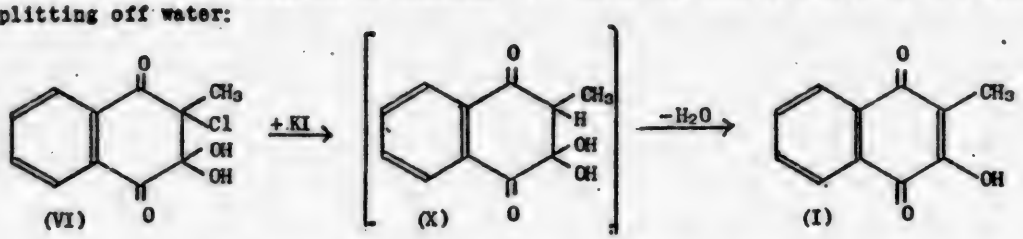
* To be sure, only 50% of the iodine separates out in these cases, for reasons that will be further examined later on.

possessing oxidizing power should take place according to the following equation under the conditions specified above:

$$RCl + 2KI + HX = RH + I_2 + KCl + KX, \text{ where } X = OH,\ Cl,\ OOCCH_3.$$

Hence, in this case, if compound (VI) really possesses a bicyclic structure, this reaction ought to result in the formation of compound (X), which can then be converted into phthiocol (I) by splitting off water:




We isolated the latter in all cases after titrating back the iodine with hyposulfite. It is obtained in very pure form in quantities that almost correspond with the iodine formed. The properties described and, especially, the fact of the nearly quantitative isolation of phthiocol (I) indicate in all probability the bicyclic structure of compound (VI).

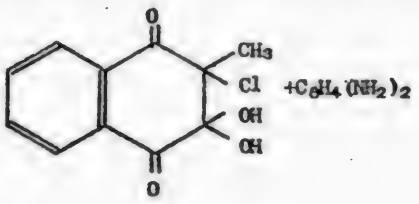
The oxidizing power of the chlorine atom in compound (VI) is manifested not only with respect to potassium iodide. As we determined, compound (VI) may be easily converted into phthiocol by means of other reducing agents as well — hydrogen sulfide, bivalent iron salts, and nascent hydrogen ($Mg + H_2SO_4$). We usually carried out this reaction in a solution of water or acetone, either in the cold or upon heating, the reaction taking place with varying speed that depends on the nature of the reducing agent used and the process conditions.

The reactions occurring between compound (VI) and potassium iodide when they are effected in a water or acetone solution require consideration in detail. If it is carried out in the absence of a mineral acid, only about 50% of iodine and phthiocol are isolated, whereas the addition of 1-2 moles of hydrochloric acid results in the isolation of iodine and phthiocol in quantities that are close to the theoretical value. This fact, for which we could find no satisfactory explanation at the start, turned out to be fully comprehensible after the relationship of the initial compound (VI) to alkaline solutions had been determined. As has already been noted above, compound (VI) is extremely sensitive to alkalis, instantaneously undergoing hydrolytic cleavage in their presence. The acids (VII) and (IX) formed as a result of this transformation are then neutralized by the base, being converted into the corresponding salts. When this same compound (VI) reacts with potassium iodide, an alkali is formed as a result of the reaction, one molecule of caustic soda being obtained for each molecule of compound (VI) and each two molecules of potassium iodide. The nascent base enters into reaction with the as yet unreacted molecules of compound (VI), splitting it into the corresponding acids and then neutralizing the latter. Naturally, the quantity of alkali formed will determine the quantity of the compound (VI) that reacts with the potassium iodide. On the other hand, inasmuch as the base is neutralized during the process of cleaving compound (VI), the hydrolytic cleavage reaction will cease until new alkali is formed as a result of the first reaction. Hence, we are dealing with two processes here: the reaction of compound (VI) with potassium iodide, on the one hand, and with the alkali formed during this first reaction, on the other. The second process takes place more rapidly than the first. Thus it becomes understandable why the reaction of compound (VI) with potassium iodide is only 50% effective in the absence of mineral acid. In the presence of the mineral acid it proceeds normally because the alkali formed in the course of the reaction is neutralized by the acid present. This likewise eliminates the possibility of the hydrolytic cleavage of compound (VI), which takes place instantaneously in the cold only in the presence of a base.

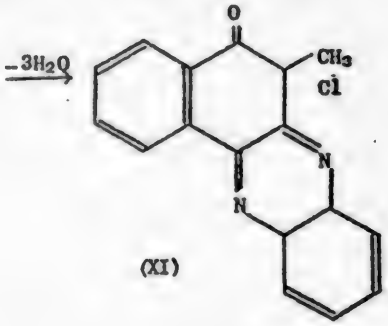
The correctness of the foregoing assertions was likewise confirmed by the fact that when these reactions were carried out in the presence of mineral acid, we isolated 100% of phthiocol (I), whereas when no mineral acid was present, only about 50% of the latter was formed, but at the same time we succeeded in obtaining about 15% of acid (VII) and about 15% of acid (IX),

which should have been formed under these conditions. Thus, the reaction of compound (VI) with potassium iodide in an aqueous or acetone solution with no mineral acid present comprises two processes, the first of which governs the basic feasibility and extent of the second process, while at the same time limiting the second process.

In a further effort to confirm the structure of compound (VI), we undertook the preparation of its quinoxaline derivative. As was to have been expected, compound (VI) reacts easily with ortho phenylene diamine, splitting off three molecules of water. The analytical data of the substance isolated correspond to formula (XI). This fact indicates the presence of two carbonyl groups side by side in the initial molecule, one of which had to be hydrated. It was worthy of note that condensing compound (VI) with ortho phenylene diamine did not affect the oxidizing power of the chlorine atom — the quinoxaline derivative (XI) formed did not lose its ability to oxidize potassium iodide to free iodine when heated in an acetic-acid solution.




(VI)




(XI)

Lastly, quite essential in proving the position of the substituents in compound (VI) is its simultaneous convertibility into ortho (α-chloropropionyl)-phenyl-glyoxylic acid (VII) and ortho lactyl-phenyl-glyoxylic acid (IX), inasmuch as this proves the nature and the position of each of its substituents. Since this conversion is bound up with the hydrolytic cleavage of the cyclic groups between the 2 and 3 carbon atoms, while the carboxyl group is formed from the carbonyl group located at position 3, it follows that it is this carbonyl group that is hydrated in the initial compound (VI).

The ortho lactyl-phenyl-glyoxylic acid (IX) obtained as a result of this reaction was investigated at length previously [9]. Its structure has been fully proven. This is not the case with ortho (α-chloropropionyl)-phenyl-glyoxylic acid (VII), which has not been described in the literature as yet. Though the structure of the initial compound (VI) and the method of preparing acid (VII) made the structure of the latter evident enough, we still thought it necessary to confirm it by further investigation.

Ortho(α-chloropropionyl)-phenyl-glyoxylic acid (VII) is best prepared by allowing a slight excess of an aqueous solution of ammonia to act upon compound (VI) in the cold. When the solution thus obtained is acidulated, a white crystalline deposit settles out; this is then purified by a single recrystallization from dichloroethane or water. The yield is 70%. The acid (VII) thus prepared fuses at 96°; it contains one molecule of water of crystallization, which is best removed by boiling the substance in dichloroethane. The anhydrous acid fuses at 147°. After recrystallization from water it is reconverted into a substance with a m.p. of 96°. Both compounds yield the same silver salt, containing no water of crystallization, and are converted into the same semicarbazone with a m.p. of 231°. The analytical data for these substances correspond to formula (VII). The titration data indicate the presence of one carboxyl group in the molecule.

Acid (VII) differs from its isomer, compound (VI), in that it does not form the corresponding ortho quinoxaline derivative when treated with ortho phenylene diamine. When treated

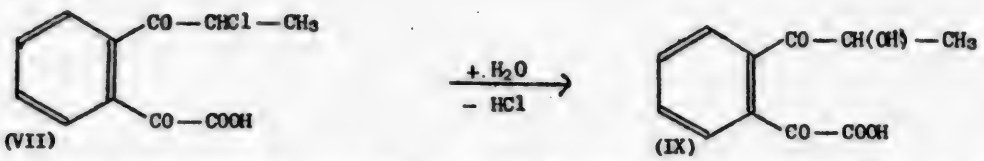
with semicarbazide in an aqueous solution, it slowly forms a semicarbazone with a m.p. of 231°• the properties of which differ from the semicarbazone prepared from compound (VI) and having a temperature of decomposition of 117–118°. Acid (VII) is sharply distinguished from compound (VI) by still another property — its chlorine atom does not possess oxidizing power and differs from the chlorine atom in compound (VI) by not oxidizing potassium iodide. The replacement of the chlorine atom by a hydroxyl group in acid (VII) likewise occurs much more slowly than is the case in compound (VI) (cf. Paper VIII [18] for details). Thus acid (VII) differs in many respects from compound (VI).

The following two reactions are most essential in verifying the structure of acid (VII):

1) Replacement of the halogen atom by a hydroxyl group, resulting in the formation of the ortho lactyl-phenyl-glyoxylic acid (IX) described earlier;

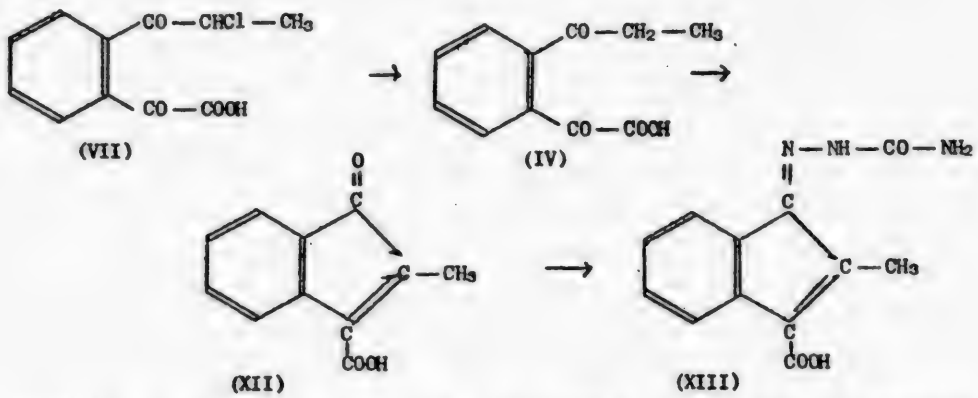
2) Replacement of the halogen atom by hydrogen, similarly resulting in the formation of the already known ortho propionyl-phenyl-glyoxylic acid (IV).

The first reaction may be effected by boiling the acid (VII) with water for a long time. To be sure, this process is very slow, inasmuch as only 10–15% of acid (VII) can be converted into ortho lactyl-phenyl-glyoxylic acid (IX) after 10 hours of boiling. This reaction is fundamental, however, in so far as it furnishes a wholly clear picture of the nature and the reciprocal positions of all the groups in the molecule of acid (VII), inasmuch as the structure of acid (IX) was clearly outlined earlier [9].



(VII) (IX)

The second reaction— the replacement of the halogen atom of the acid (VII) by hydrogen — takes place during the reduction of this acid by magnesium in the presence of a 10% solution of sulfuric acid. The ortho propionyl-phenyl-glyoxylic acid (IV) formed as the result of this reduction is obtained together with other reaction products, which impede its purification considerably. We therefore did not isolate it in pure form, but immediately converted it after isolation from the solution into the easily identifiable 2-methyl-indenone-1-carboxylic acid-3 (XII) or into the semicarbazone of the latter (XIII). The structure of the two latter compounds and the process of their preparation from ortho propionyl-phenyl-glyoxylic acid (IV) were investigated in detail earlier [9]; hence their isolation as end products fairly well justifies the assumption that the acid (IV) actually is the primary product of the reduction of acid (VII).



(VII) (IV) (XII) (XIII)

• It should be noted that this semicarbazone is not a derivative of the acid (VII). Its genesis is bound up with a series of profound transformations of the initial molecule. This problem is dealt with in detail in Paper IX [9a]

Likewise characteristic of acid (VII) is its ability to undergo a series of transformations upon heating with aqueous solutions of alkalis, resulting in the formation of new five- and six-membered rings. Communication IX [63] is especially devoted to these reactions, and we shall therefore not dwell upon them in detail at this point.

In conclusion, it should be pointed out that the chlorotriketone (V) described above and its hydrated form (VI) are of interest in that they may serve as raw materials for the synthesis of other substituted triketones of the tetrahydronaphthalene series. Some of the research done by us in this field is set forth in our following communication [16].

## EXPERIMENTAL*

### I. SYNTHESIS AND PROPERTIES OF 2-CHLORO-2-METHYL-1,2,3,4-TETRAHYDRONAPHTHALENEDIOL-3,3-DIONE-1,4 (VI)

1. Preparation. 2 g of phthiocol (m.p. 172°) are carefully comminuted in a mortar with 10-15 ml of water, and a moderate current of chlorine is allowed to pass through the suspension thus prepared for 6-8 hours. The mass, which is yellow to begin with, gradually grows lighter and ends up almost white. After the chlorine stream is turned off, the deposit is filtered out, washed with water until all chlorine ions are removed, and air-dried. Weight: 2.3 g. Yield: 90%. A white crystalline substance with a m.p. of 102.-103° is obtained after 1-2 recrystallizations from 6-7 ml of benzene, using bone black. The substance dissolves with difficulty in cold water, but is easily soluble in alcohol, ether, acetone, benzene, and hot water**. It dissolves rather quickly in an aqueous solution of soda and instantaneously in aqueous solutions of caustic alkalis; the alkaline solution, colorless to begin with, rapidly yellows and then turns red, becoming dark red upon heating.

| | | |
|---|---|---|
| | Found %: | C 54.79; H 3.74; Cl 15.13. |
| $C_{11}H_9O_4Cl$. | Calculated %: | C 54.88; HH 3.74; Cl 14.76. |

The number of active hydrogen atoms, determined by the Tserevitinov-Terentyev method [64], equaled 2.93.

Determination of water. A weighed portion of the substance is heated in vacuum at 6 mm and 125-130° until the weight remains constant.

| | | |
|---|---|---|
| | Found %: | $H_2O$ 7.49 |
| $C_{11}H_7O_3Cl \cdot H_2O$. | Calculated %: | $H_2O$ 7.48. |

See Tables 1 and 2 for behavior in the presence of alkali.

2. Dehydration. 2 g of the hydrated chlorotriketone (VI) (m.p. 102-103°) are distilled from a 5 ml Cluizen flask. Water is driven off at 125° and 6 mm. The water is eliminated from the receiver by means of external heating. The 2-chloro-2-methyl-1,2,3,4-tetrahydronaphthalene--1,3,4-trione (V) is distilled over at 168-170° and 6 mm. The substance distills over as a yellow, very viscous oil. Weight: 1.6 g. Yield: 86%. It is extremely hygroscopic. Taking a weighed portion was rather difficult in spite of all precautionary measures.

| | | |
|---|---|---|
| | Found %: | C 58.82; H 3.13. |
| $C_{11}H_7O_3Cl$. | Calculated %: | C 59.32; H 3.15 |

This substance may also be prepared by prolonged boiling of a benzene solution of the hydrated chlorotriketone (VI), followed by driving off the benzene; a yellow oil is left behind, which is then purified by vacuum distillation.

Moreover, this chlorotriketone (V) is formed directly from phthiocol by the chlorination of the latter in a medium of absolute carbon tetrachloride. But in this case the isolation of the substance and its preparation in pure form involve considerable difficulties.

*The analytical section of the research was carried out with the assistance of E. A. Ignatyeva, to whom we express our appreciation.

**The substance changes when heated with water; see below for details.

TABLE 1

Titration Data in a 50% Alcohol Medium

| Weight of substance (g) | N/10 NaOH (ml) | | N/10 $AgNO_3$ (ml) | | Chlorine found % | Remarks |
|---|---|---|---|---|---|---|
| | Found | Calculated | Found | Calculated | | |
| 0.1710 | 6.73 | 7.11 | 0.90 | 7.11 | 12.66 | * |
| 0.1484 | 6.12 | 6.13 | 0.82 | 6.13 | 13.88 | ** |
| 0.1435 | 11.60 | 11.94 | 5.07 | 5.97 | 84.93 | *** |

3. Hydration of the chlorotriketone (V). 0.25 g of freshly distilled substance is added to 3 ml of water. When the oil is added to the water, white crystals form immediately upon the surface. When stirred with a glass rod, all the oil crystallizes within a few minutes. The substance obtained is filtered out and dried in the air. M.p 102°. A sample, mixed together with the hydrated chlorotriketone (VI), melts at the same temperature. Yield is quantitative.

4. Reaction of the hydrated chlorotriketone (VI) with ortho phenylene diamine. 2 g of the substance is dissolved in 4 ml of hot benzene and mixed with a solution of 1.4 g of ortho phenylene diamine (1.5 moles) in 8 ml of hot benzene. The mixture boils up immediately. The solution grows cloudy because of the water that separates out as a result of the reaction, at the same time turning dark brown in color. As it cools a yellow crystalline precipitate settles

TABLE 2

Titration Data in a 50% Acetone Medium

| Weight of substance (g) | N/10 NaOH (ml) | | N/10 $AgNO_3$ (ml) | | Chlorine found % | Remarks |
|---|---|---|---|---|---|---|
| | Found | Calculated | Found | Calculated | | |
| 0.1674 | 8.59 | 6.99 | 1.65 | 6.99 | 23.71 | * |
| 0.1800 | 8.88 | 7.48 | 1.50 | 7.48 | 20.06 | ** |
| 0.1595 | 13.50 | 12.78 | 5.35 | 6.39 | 80.69 | *** |

out. It is filtered out, quickly washed with benzene, and immediately dried in vacuum at 5 mm and 50°, since the wet precipitate changes when exposed to air very quickly, turning from yellow to violet gray in color. Weight: 2.2 g (yield 92%); m.p. 161-163°.

The quinoxaline derivative of the chlorotriketone (XI) is heated with 15-20 ml of alcohol until almost the boiling point is reached, and the dark-red solution is decanted from the undissolved precipitate. The latter is twice recrystallized from a considerable quantity of alcohol, animal charcoal being used. Nearly white needles with a m.p. of 167° are obtained. When exposed to light for a long time or to direct sunlight, the substance rapidly turns a brick-red color, without changing the melting point, however.

$C_{17}H_{11}ON_2Cl$. Found %: C 69.58; H 3.65; N 9.42.
Calculated %: C 69.27; H 3.73; N 9.51.

When the chlorotriketone (V) is acted upon by ortho phenylene diamine under the same conditions, the same quinoxaline derivative with a m.p. of 167° is obtained.

5. Reaction of the hydrated chlorotriketone (VI) with semicarbazide. 2 g of the substance is dissolved, with heating, in 20 ml of alcohol and, upon cooling, are mixed with a solution of

* Titrated back with N/10 solution of NaOH and chlorine immediately determined by the Volhard method.
** Titrated back with N/10 solution of NaOH and chlorine determined 1 hour later.
*** Three weight equivalents of N/10 solution of NaOH added; 1 hour later the excess of alkali is titrated back with N/10 $H_2SO_4$, and the chlorine determined by the Volhard method.

2 g of semicarbazide hydrochloride and 2 g of crystalline potassium acetate in 20 ml of water. The crystallization of the semicarbazone formed commences within a few minutes. The next day the precipitate is filtered out, washed with alcohol, water, and alcohol again, and then air-dried. Weight: 2.1 g. M.p: 114-116° (decomp.). The crystals are large flakes in the form of true parallelograms. The semicarbazone formed is insoluble in ether, benzene, ethyl acetate, dichloroethane, and carbon tetrachloride, and soluble with difficulty in hot water; a yellow tarry substance separates out, however, upon cooling. It can be recrystallized from methyl alcohol if prolonged heating of the alcohol solution is avoided. M.p.: 117-118° (decomp.).

| | | |
|---|---|---|
| | Found %: | C 48.39; H 4.37. |
| $C_{12}H_{12}O_4N_3Cl$. | Calculated.%: | C 48.40; H 4.84 |

6. Hydrolytic cleavage of the hydrated chlorotriketone (VI) by water. 1 g of the substance is boiled with 20 ml of water for 15 minutes in a flask fitted with a reflux condenser. As heating begins, the substance melts and then quickly dissolves in the water. After boiling is completed, the solution is cooled, and the extremely minute quantity of light yellow tar (about 0.03 g) is filtered out. The filtrate is twice extracted with ether. The ether solution is dried with sodium sulfate, and the ether is then driven off. Traces of the latter are eliminated in vacuum. What is left is a viscous oil, which gradually crystallizes completely after a priming tube is introduced. Weight: 0.55 g. Yield: 51%. The substance is ground up in the cold with 0.5 ml of dichloroethane, filtered, washed with a few drops of this solvent, and recrystallized from 1.5 ml of dichloroethane. M.p.: 95-96°. A sample, mixed with ortho (α-chloropropionyl)-phenyl-glyoxylic acid,* melts at the same temperatures.

After extraction of the ether the aqueous solution was evaporated to dryness at 5-10 mm and 15°. What is left is a white crystalline substance (weight: 0.3 g), which is twice crystallized from a very small quantity of water. M.p.: 230-232° (decomp.). A sample, mixed with ortho lactyl-phenyl-glyoxylic acid (IX), fuses with decomposition at the same temperature. Yield: 32%.

## II. INVESTIGATION OF THE OXIDATIVE ABILITY OF THE CHLORINE IN 2-CHLORO-2-METHYL-1,2,3,4-TETRAHYDRONAPHTHALENEDIOL-3,3-DIONE-1,4 (VI).

1. Determination of the oxidative ability of chlorine.

a) By the K. Meyer method [62]. A weighed portion, 0.1-0.2 g, of the substance is dissolved in 15 ml of alcohol, and 10 ml of concentrated hydrochloric acid and an excess of potassium iodide (0.4-0.8 g, depending upon the size of the weighed portion) are added. The solution is at once colored red. The reaction mixture is heated for 15 minutes at 70°. During heating the color of the solution turns brownish red. After cooling it is diluted with water (up to 100-125 ml), and the iodine that separates out is titrated back with N/10 solution of hyposulfite. Iodine found (in %): 99.48; 100.83; 97.44. All three tests are combined, and the yellow crystalline deposit that settles out is filtered out 24 hours later, washed with water, and dried in air. M.p.: 171-172°. A sample, mixed with phthiocol, fuses at the same temperature. Yield: 98%.

b) By the Whiteley method [60, 61]. 0.1497 g of the substance is dissolved in 15ml of glacial acetic acid, and 0.5 g of potassium iodide. The iodine that separates out causes the solution to turn light brown at once. It is heated for 15 minutes at 90°. The color of the solution turns dark brown. After cooling the reaction mixture is diluted with 30-40 ml of water, and the iodine liberated is titrated back with a N/10 solution of hyposulfite. Iodine found (in %): 103.88. The yellow crystalline deposit that settles out when the solution is diluted with water is filtered out 24 hours later, washed with water, and air-dried. M.p.: 171-172°. A sample mixed with phthiocol fuses at 172°. Weight: 0.12 g. Yield: 102.5%.

2. Reduction by iron sulfate. To 0.5 g of the hydrated chlorotriketone (VI) dissolved in 5 ml of acetone there are added 3 ml of concentrated hydrochloric acid and a solution of 5 g of ferrous sulfate in 10 ml of water. The solution obtained is boiled for 30 minutes in a flask fitted with a reflux condenser. The solution turns brown, and a yellow crystalline deposit

* Its preparation and properties are described below in Experiments III, 1-4.

gradually settles out. After the reaction mass cools, the deposit is filtered out, washed with water, and dissolved in 8 ml of a 10% soda solution. The dark-red solution is extracted with ether and then acidulated with hydrochloric acid. The deposit that settles out is filtered out, washed with water, and air-dried. M.p.: 172-173°. A sample mixed with phthiocol fuses at 172-173°. Weight: 0.15 g. Yield: 40%.

When this experiment is carried out under all the conditions set forth above, but with mineral acid eliminated, the yield of the phthiocol formed is 27%. If the reaction is effected at room temperature, no phthiocol is formed, whether mineral acid is present or not.

3. Reduction by magnesium in sulfuric acid. 0.5 g of the hydrated chlorotriketone (VI) is dissolved in 10 ml of acetone, and 100 ml of 10% sulfuric acid. Then 3.5 g of magnesium chips are gradually added during 5 hours, care being taken that the temperature of the solution is kept within the range of 15-18°. The solution turns yellow fairly quickly, and a yellow deposit of phthiocol gradually settles out. It is filtered out, washed with water, and air dried. The acetone is removed from the filtrate by heating in vacuum, the solution then being extracted with ether. The ether extract is washed with a 10% soda solution, the soda solution then being acidulated with 10% hydrochloric acid. The precipitate that settles is filtered out, washed with water, dried in air, and combined with that prepared earlier. M.p.: 171-172°. A sample mixed with phthiocol fuses at the same temperature. Weight: 0.33 g. Yield: 88%.

4. Reduction by hydrogen sulfide. 0.5 g of the hydrated chlorotriketone (VI) is dissolved in 10 ml of acetone; after adding 10 ml of water, a stream of hydrogen sulfide is passed through for 1 hour. A bright-yellow crystalline deposit settles out; it is filtered, washed with water, and dried in air. Weight: 0.45 g. The deposit obtained is dissolved in 20 ml of a 10% soda solution and twice extracted with carbon disulfide to remove the sulfur. The dark red solution is then acidulated with 10% sulfuric acid, and the yellow precipitate that settles is filtered out, washed with water, and air-dried. M.p.: 172°. A sample mixed with phthiocol fuses at 172°. Weight: 0.35 g. Yield: 93.5%.

After elimination of the carbon disulfide, 0.1 g of sulfur, produced by the oxidation of the hydrogen sulfide by the hydrated chlorotriketone (VI), is isolated from the carbon-disulfide solution.

5. Reaction of the hydrated chlorotriketone (VI) with potassium iodide in acetone.

a) Determination of iodine and phthiocol. 0.2162 g of the substance is dissolved in 30 ml of acetone, and an excess of potassium iodide (about 0.6 g) is added. Iodine begins to separate out at once. The reaction mixture is allowed to stand for 1 hour at room temperature, then diluted with an equal volume of water, and the iodine set free is titrated back with a N/10 solution of hyposulfite. The yellow precipitate that settles is filtered out, washed with water, and dried in air. M.p.: 171-173°. A sample mixed with phthiocol fuses at the same temperature. Iodine found (in %): 54.95. Yield of phthiocol (in %): 56.2.

b) Isolation of ortho lactyl-phenyl-glyoxylic acid. The reaction was carried out under the same conditions as the previous experiment. Taken: 1 g of the substance, 30 ml of acetone, and 2 g of potassium iodide. After completion of the reaction 0.5 liter of water is added, and the iodine liberated is reduced by hyposulfite. After the lapse of 24 hours, the deposit of phthiocol that settles out is filtered, washed with water, and dried in air. Weight 0.43 g. Yield: 55%. M.p.: 172°.

The filtrate is concentrated to a volume of 150 ml at 10 mm and 30° and then twice extracted with ether, after which it is evaporated at 10 mm and 30° to dryness. The solid residue is treated several times with cold benzene and then extracted with ether for 5-6 hours in a Soxhlet apparatus. After the ether has been removed, there remains 0.2 g of a light-yellow substance with a m.p. of 220° (decomp.). It is then twice recrystallized from a very minute quantity of water. White crystals with a m.p. of 232° (decomp.) are obtained, which fuse at the very same temperature when mixed with ortho lactyl-phenyl-glyoxylic acid (IX). Yield: 21.5%.

c) Isolation of ortho (α-chloropropionyl)-phenyl-glyoxylic acid. The reaction conditions and the quantity of reagents are the same as in the preceding experiment. Upon conclusion of the reaction the acetone is driven off at 10 mm at 20°. To the dark-brown residue there is added 25 ml of a N/10 solution of sulfuric acid, and the iodine is reduced by a concentrated solution of hyposulfite, avoiding an excess of the latter. The deposit of phthiocol that settles is filtered out, and the aqueous solution is extracted with ether three times. The ether solution is dried with sodium sulfate, and the ether is driven off. There remains a yellow crystalline substance, which is treated with cold carbon disulfide and then twice recrystallized from dichloroethane. We obtain 0.12 g of white crystals with a m.p. of 96°. A sample, mixed with ortho(α-chloropropionyl)-phenyl-glyoxylic acid, fuses at the same temperature. Yield: 12%.

6. Reaction of the hydrated chlorotriketone (VI) with potassium iodide in an aqueous solution.

a) In the absence of acid. About 0.15 g of the substance is placed in a solution of 0.4 g of potassium iodide in 10 ml of water. Iodine begins to separate out at once, the substance gradually converting to phthiocol. The reaction mixture is allowed to stand for 1.5 hours, with periodic shaking, after which the iodine is titrated back with a N/10 solution of hyposulfite. The next day the deposit of phthiocol is filtered out, washed with water, and dried in air. M.p.: 171-172° (from methyl alcohol). Iodine found (in%): 47.98; 46.34. Phthiocol isolated (in %): 54.42; 53.01.

b) In the presence of acid. The reaction conditions are the same as in the preceding experiment, with the sole difference that the potassium iodide is not dissolved in water, but in a N/10 solution of hydrochloric acid, which in the first case is taken in a weight-equivalent quantity, and in twice that quantity in the second. The external reaction proceeded as in the foregoing experiment. The determination of iodine and phthiocol was effected as described above. Iodine found (in %): 88.56; 89.90. Phthiocol isolated (in %): 101.91; 100.54.

7. Reaction of the quinoxaline derivative of the chlorotriketone (XI) with potassium iodide. 0.1640 g of the substance is dissolved in 25 ml of glacial acetic acid, with heating, 1.0 g of potassium iodide is added, and the whole is heated to 90-100° for 15 minutes. After cooling, 35 ml of water are added, and the red precipitate formed during the reaction is filtered out. It is then washed with water, alcohol, and again water until all traces of iodine disappear from the wash water. The compound obtained contains no halogen; it does not fuse when heated to 300°. Weight: 0.15 g. The iodine in the filtrate, combined with the wash waters, is determined by titration with a N/10 solution of hyposulfite. Iodine found (in %): 105.9%. It should be noted that the quinoxaline derivative of the chlorotriketone (XI) remains unchanged when subjected to the conditions of the foregoing experiment in the absence of potassium iodide.

III. METHODS OF PREPARATION AND PROPERTIES OF ORTHO (α-CHLOROPROPIONYL)-PHENYL-GLYOXYLIC ACID.

1. Methods of Preparation.

a) Action of sodium thymolate. 1 g of the hydrated chlorotriketone (VI) is dissolved in 25 ml of absolute ether, and a 0.5% solution of sodium thymolate (10% excess) in absolute ether is added. A white gelatinous deposit of the sodium salt of ortho (α-chloropropionyl)-phenyl-glyoxylic acid immediately settles out; it is filtered out after 10-15 minutes through a Schott funnel No. 2 and washed 2-3 times with absolute ether. Filtration is done slowly, the deposit gradually reddening as time goes on. The substance is dissolved quickly in 3-4 ml of water and extracted once with a small quantity of ether; the aqueous solution is passed through a filter and acidulated with 1.5 ml of concentrated sulfuric acid; this causes a yellow oil to settle out, which gradually crystallizes. The acid obtained is twice recrystallized from a small quantity of dichloroethane in the presence of animal charcoal. M.p.: 86-88°. Weight: 0.8 g. Yield: 74%.

It should be noted that this method does not produce a sufficiently pure ortho (α-chloropropionyl)-phenyl-glyoxylic acid in spite of the repeated recrystallizations. For this reason the method outlined below is much more satisfactory.

b) Action of ammonia. 10 g of the hydrated chlorotriketone (VI) are carefully triturated with 35 ml of water, after which 20 ml of a 10% aqueous solution of ammonia is added in small portions until the solution is weakly alkaline; this results in the gradual dissolution of the initial compound. The pale pinkish solution produced is filtered to remove any undissolved residue and then acidulated with 10 ml of 15% hydrochloric acid. The crystalline white precipitate is filtered out, washed with a small quantity of water, and dried in air. M.p.: 92-93°. Weight: 7.2 g.

The aqueous solution is combined with the wash waters and extracted twice with ether. The ether solution is dried with sodium sulfate, boiled with animal charcoal, and the ether driven off, the final traces of the latter being eliminated in vacuum. There remains 0.6 g of a rapidly crystallizing oil. The substance is combined with that previously prepared and recrystallized from 15 ml of dichloroethane, animal charcoal being added. White crystals of ortho (α-chloropropionyl)-phenyl-glyoxylic acid, with a m.p. of 95-96°, are obtained. Yield: 72%.

After extraction with ether an aqueous solution is evaporated at 10 mm and 20° to dryness, and the dry residue is extracted with ether for 20 hours in a Soxhlet apparatus. After the ether is eliminated, there remains 0.7 g of the substance, which is twice recrystallized from a small quantity of water, animal charcoal being used. M.p.: 230-232° (decomp.). When mixed with ortho lactyl-phenyl-glyoxylic acid the substance fuses with decomposition at the same temperature. Yield: about 10%.

It was interesting to compare the data cited for the conditions of the hydrolytic cleavage of the hydrated chlorotriketone (VI) with the behavior of phthiocol in aqueous solutions of alkalis. We dissolved the latter in ten times its volume of a 10% aqueous solution of caustic soda. After 6 hours had elapsed, the solution was acidulated, as a result of which unchanged phthiocol, with a m.p. of 172-173°, was recovered quantitatively. Hence, under these conditions phthiocol undergoes no change, thus differing from the hydrated chlorotriketone.

2. Properties of ortho(α-chloropropionyl)-phenyl-glyoxylic acid. This substance consists of flat white rectangular flakes with a m.p. of 96°. It crystallizes from water with 1 molecule of the solvent. The water of crystallization can be expelled by boiling the substance twice with dichloroethane. The compound that crystallizes out after cooling no longer contains a molecule of water of crystallization and is in the form of flat hexagonal flakes with a m.p. of 147°. This compound is again converted into the substance with a m.p. of 96° after recrystallization from water. Both substances dissolve very easily in cold acetone, glacial acetic acid, ethyl acetate, and ethyl alcohol. They crystallize easily out of dichloroethane, tetrachloroethane, nitrobenzene, and water. They dissolve in an aqueous solution of alkali, turning the solution yellow, and turning red upon heating. They dissolve with the liberation of carbonic acid in an aqueous solution of soda.

Substance with m.p. of 96°.

| | | | | |
|---|---|---|---|---|
| | Found %: | C 51.07; | H 4.18; | Cl 14.07. |
| $C_{11}H_9O_4Cl \cdot H_2O$. | Calculated %: | C 51.06; | H 4.25; | Cl 13.73 |

Substance with m.p. of 147°.

| | | | | |
|---|---|---|---|---|
| | Found %: | C 55.10; | H 3.76; | Cl 15.03. |
| $C_{11}H_9O_4Cl$. | Calculated %: | C 54.88; | H 3.74; | Cl 14.76. |

Determination of water. The substance with a m.p. of 96° was dried at 100-105° and 3-5 mm until its weight remained constant.

| | | |
|---|---|---|
| | Found %: | $H_2O$ 6.97. |
| $C_{11}H_9O_4Cl \cdot H_2O$. | Calculated %: | $H_2O$ 6.96. |

Investigation of the oxidizing power of the chlorine atom. The reaction was carried out under the conditions of Experiment II, 1a (by the K. Meyer method), Experiment II, 1b (by the Whitely method), and Experiment II, 5 (in a solution of acetone in the presence of potassium iodide). In each case the results were negative, indicating that the chlorine atom in the substance possesses no oxidizing power.

Behavior of ortho (α-chloropropionyl)-phenyl-glyoxylic acid in the presence of an alkali. Cf. Tables 3 and 4.

Reaction with ortho phenylene diamine. When the reaction is carried out under the conditions described in Experiment I, 4, we get nothing but a viscous yellow-brown tarry product that darkens upon exposure to light. In this case no individual compound is formed.

3. Preparation of the silver salt of ortho (α-chloropropionyl)-phenyl-glyoxylic acid. 0.75 g of the acid with a m.p. of 96°* is triturated with 7.5 ml of water, after which about 1 ml of a 10% solution of ammonia is added until the solution turns weakly alkaline; nearly all the substance dissolves thereby. The medium is rendered neutral or slightly acid by the addition of a small amount of ortho (α-chloropropionyl)-phenyl-glyoxylic acid. A few drops of a 10% solution of silver nitrate are added to the solution and the slight precipitate formed is filtered out. Then 7.5 ml of 10% silver nitrate solution are added to the transparent filtrate. Soon a white crystalline deposit of the silver salt settles out. The latter is filtered out, washed with a small amount of water and then with alcohol and ether, and dried at 10 mm and 20°. Weight: 0.95 g. Yield: 95%.

Found %: C 38.03; H 2.09
$C_{11}H_8O_4ClAg$. Calculated %: C 37.99; H 2.30.

4. Conversion of ortho(α-chloropropionyl)-phenyl-glyoxylic acid (VII) into ortho lactyl--phenyl-glyoxylic acid (IX). 2 g of the substance are boiled for 2 hours with 25 ml of water in a flask fitted with a reflux condenser. The cooled solution is extracted two times with ether, the ether solution is dried with sodium sulfate, and the ether is expelled. The final traces of the latter are driven off in vacuum. There remains a thick oil, which rapidly crystallizes. Weight: 1.82 g. M.p.: 94-95°. A sample mixed with the initial acid melts at the same temperature. After extraction with ether, an aqueous solution is evaporated to dryness

TABLE 3

Titration data in a 50% alcohol medium

| Weight of substance (g) | N/10 NaOH (ml) | | N/10 $AgNO_3$ (ml) | | Chlorine found (%) | Remarks |
|---|---|---|---|---|---|---|
| | Found | Computed | Found | Computed | | |
| 0.0955 | 3.72 | 3.69 | 0.08 | 3.69 | 2.27 | •• |
| 0.1659 | 6.46 | 6.42 | 0.10 | 3.42 | 1.56 | ••• |
| 0.1503 | 11.72 | 11.62 | 5.71 | 5.81 | 98.3 | •••• |

at 3 mm and 25°. There remains 0.08 g of a white crystalline substance, which fuses at 230-232° after recrystallization from a very minute quantity of water, animal charcoal being used, and exhibits no melting-point depression when mixed with ortho lactyl-phenyl-glyoxylic acid (IX).

TABLE 4

Titration data in a 50% acetone medium

| Weight of substance (g) | N/10 NaOH (ml) | | N/10 $AgNO_3$ (ml) | | Chlorine found (%) | Remarks |
|---|---|---|---|---|---|---|
| | Found | Computed | Found | Computed | | |
| 0.1638 | 6.41 | 6.34 | 0.15 | 6.34 | 2.36 | •• |
| 0.1843 | 7.21 | 7.15 | 0.15 | 7.15 | 2.10 | ••• |
| 0.2242 | 17.35 | 17.34 | 8.57 | 8.67 | 98.85 | •••• |

*The anhydrous acid, with a m.p. of 147°, may also be used in the preparation of the silver salt.
**Titrated back with N/10 solution of NaOH and chlorine immediately determined by the Volhard method.
***Titrated back with N/10 solution of NaOH and chlorine determined 1 hour later.
****Three weight equivalents of N/10 solution of NaOH added; 1 hour later the excess of alkali is titrated back with N/10 $H_2SO_4$, and the chlorine determined by the Volhard method.

5. Reduction of ortho (α-chloropropionyl)-phenyl-glyoxylic acid (VII). 0.5 g of the substance is dissolved in 125 ml of 10% sulfuric acid and energetically reduced at 20° by the addition of 2.7 g of magnesium chips during the course of 1 hour with continuous stirring. The solution obtained is extracted with ether 5 times. The ether extract is dried with sodium sulfate, and the ether is driven off. The last traces of ether are expelled in vacuum. There remains a solid substance that is nearly white, with a m.p. of 153-156°. Weight: 0.35 g. The ortho propionyl-phenyl-glyoxylic acid (IV) thus produced is purifiable only with difficulty; hence it is more expedient not to call it such, but to convert it into 2-methyl-indenone-1-carboxylic acid-(3) (XII) and the semicarbazone of that acid. (XIII). The latter product was prepared directly from ortho propionyl-phenyl-glyoxylic acid by heating it in an aqueous solution with semicarbazide hydrochloride in the presence of potassium acetate.

Both of these compounds were prepared under the conditions described in Paper III, [8]. The former had a m.p. of 213° after crystallization from glacial acetic acid. The latter fused with decomposition at 268° after double crystallization from alcohol. Neither substance caused a depression of the melting point when mixed with the corresponding preparations produced from the ortho propionyl-phenyl-glyoxylic acid prepared by the method described in Paper III [8].

## CONCLUSIONS

In order to clarify the conditions and the nature of the hydrolytic cleavage of the 1,2,3,4-triketone of the tetrahydronaphthalene series the 2-chloro-2-methyl-substituted triketone of this type was synthesized and several of its properties and transformations were investigated. It was shown that it undergoes hydrolytic cleavage to ortho (α-chloropropionyl)-phenyl-glyoxylic acid very easily when briefly heated with water. In the presence of aqueous solutions of alkalis this process occurs almost instantaneously.

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# OXIDATIVE AND OXIDATIVE-HYDROLYTIC TRANSFORMATIONS OF ORGANIC MOLECULES

## VIII. HYDROLYTIC TRANSFORMATION OF HYDROXY- AND ACETOXYKETONES OF THE TETRAHYDRONAPHTHALENE SERIES*

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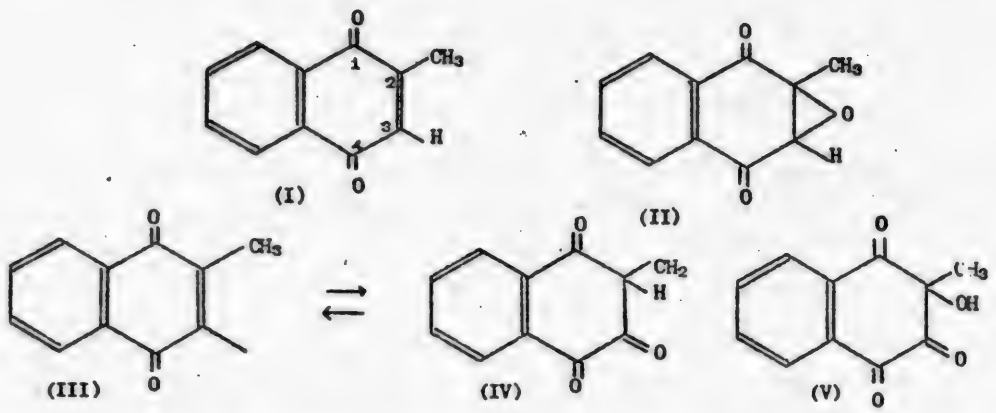
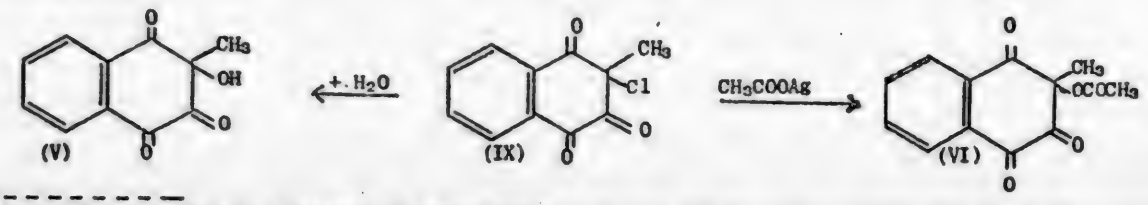
In the general plan of the experimental research undertaken by us to elucidate the causes and the mechanism of the oxidative-hydrolytic cleavage of the quinones the investigation of the hydroxytriketone (V) was of special interest. As a representative of the second degree of oxidation of the initial quinone (I), the latter should, from our point of view (set forth in detail in Paper I [1]) undergo hydrolytic transformation much more easily than its corresponding oxide (II) and hydroxyquinone (III) [a tautomeric triketone (IV)], which must be considered to be representatives of the first degree of oxidation of the initial 2-methyl-1,4-naphthoquinone (I).

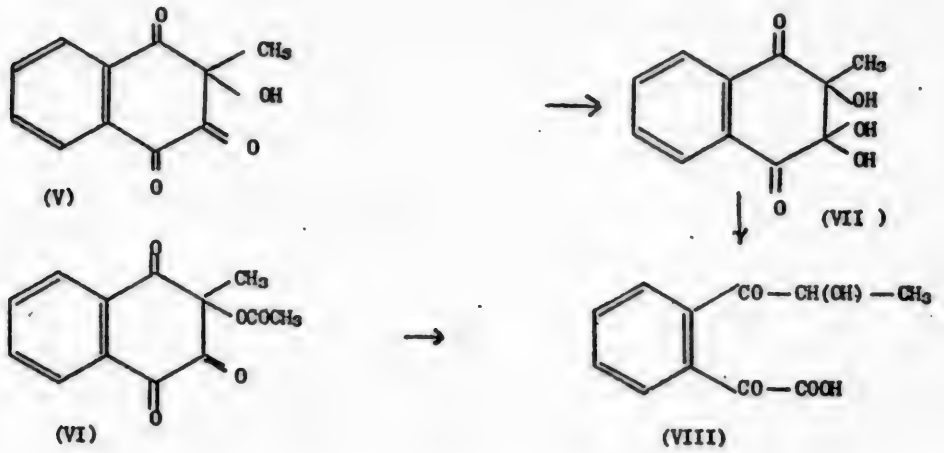


Unfortunately, hydroxytriketones of type (V) are not reported in the literature. Nor are there indications of possible methods of their synthesis. Nevertheless, it seemed to us that, starting with the chlorotriketone (IX), described in our previous paper [5], we could outline the method of preparation of the hydroxytriketone (V). And, in fact, we succeeded in converting compound (IX), first into the hydroxytriketone (V) and then into the acetoxytriketone (VI). The first of the two was prepared from the chlorotriketone (IX) by heating the latter for a brief period with water, while the second was formed by heating the latter with silver acetate (see below for details).



* Paper IX, on Hydrolytic Cleavage of Carbon Bonds.

After we had confirmed the structure of these compounds (see below) we undertook the investigation of the conditions and nature of the hydrolytic cleavage of their cyclic groups. As was to have been expected, both of them proved to be highly unstable to the action of hydrolyzing agents. When the hydroxytriketone (V) is boiled with water for 30–45 minutes, its cleavage is practically complete, forming ortho lactyl-phenyl-glyoxylic acid (VIII). This reaction occurs almost instantaneously, even in the cold, when as little as 1% of an alkaline solution is present. The acetoxytriketone (VI) behaves similarly, though somewhat longer heating with water for complete conversion to the acid (VIII) is required (about 3–4 hours) owing to the presence of the acetoxy group.



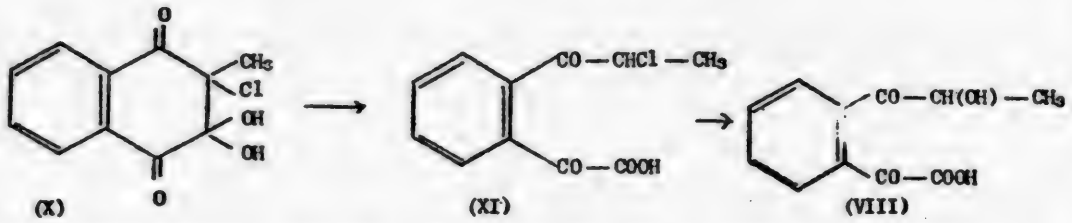

Comparison of these results with the conditions governing the cleavage of 2-methyl-1,4--naphthoquinone (I), the oxide of 2-methyl-1,4-naphthoquinone (II), and 2-methyl-3-hydroxy-1,4--naphthoquinone (phthiocol) (III) $\rightleftharpoons$ (IV) is quite instructive.

The initial quinone (I) is able to undergo only an oxidative hydrolytic cleavage. Its cyclic grouping can be split only after very long boiling with water, if the solution's pH is higher than 7, while an oxidant acts upon it at the same time [2]. Compounds (II) and (III) $\rightleftharpoons$ (IV), which are representatives of the first degree of oxidation of this quinone, are split much more easily. The oxide (II) must be boiled for a rather long time with water at a pH = 7. Even in this case, however, the cleavage of the ring is not purely hydrolytic, but is oxidative-hydrolytic [4]. As for phthiocol (III) $\rightleftharpoons$ (IV), the splitting of the bonds between the carbon atoms of the ring no longer requires the preliminary action of an oxidant, being of a purely hydrolytic character, but it takes place only upon many hours of boiling with water at a solution pH that is higher than 7, [3]. The compounds (V) and (VI) studied by us, which are representatives of the second degree of oxidation of the initial quinone (I), however, tend to undergo a purely hydrolytic cleavage under incomparably milder conditions, under which the compounds (I), (II), and (III) $\rightleftharpoons$ (IV) either remain unaffected or undergo an oxidative-hydrolytic cleavage, but not a purely hydrolytic one. It follows, therefore, that the following assertion applies to the series of compounds investigated by us: **the higher the degree of oxidation of the original quinone molecule, the easier the hydrolytic cleavage.**

It should be emphasized, moreover, that the conditions for the hydrolytic cleavage of this type of cyclic groupings can be rendered easier not only by the subsequent introduction of hydroxyl or carbonyl groups into the molecule. Any substituent that can effect the required polarization of the C—C bond between the 2 and 3 carbon atoms of para naphthoquinones will likewise facilitate these reactions. In this connection, a good illustration of what we have just said is afforded by juxtaposing the conditions for the hydrolytic cleavage of the compounds

(III) ⇌ (IV) [3], (IX) [5], and (V). It is found that replacing the hydrogen atom located at the 2 carbon atom in the tautomeric form (IV) by chlorine (compound IX) or by hydroxyl (compound V) facilitates the hydrolytic cleavage of these compounds about equally.

Let us now turn to a discussion of the methods of preparation of the hydroxytriketone (V) and the acetoxytriketone (VI), the conditions and nature of the hydrolytic cleavage of which were examined above. As has been pointed out already, they can be prepared from the chlorotriketone (IX). But to work out the methods of synthesizing these compounds we first had to investigate the reaction involving the replacement of the halogen atom in compounds (IX) and (X) by the hydroxyl or acetoxy group. It was noted [5] that when compound (X) is boiled with water for 45 minutes, it undergoes hydrolytic cleavage, being completely converted into two acids: ortho (α-chloropropionyl)-phenyl-glyoxylic acid (XI) and ortho lactyl-phenyl-glyoxylic acid (VIII). Each of these acids can be easily separated and then isolated in pure form. The first is obtained under these conditions with a yield of some 50%, while the yield of the latter is about 30%. Possessing some data concerning the properties of these compounds [5], it was natural to assume that the acid (XI) is first formed, part of it then being converted during the reaction to acid (VIII):




(X) (XI) (VIII)

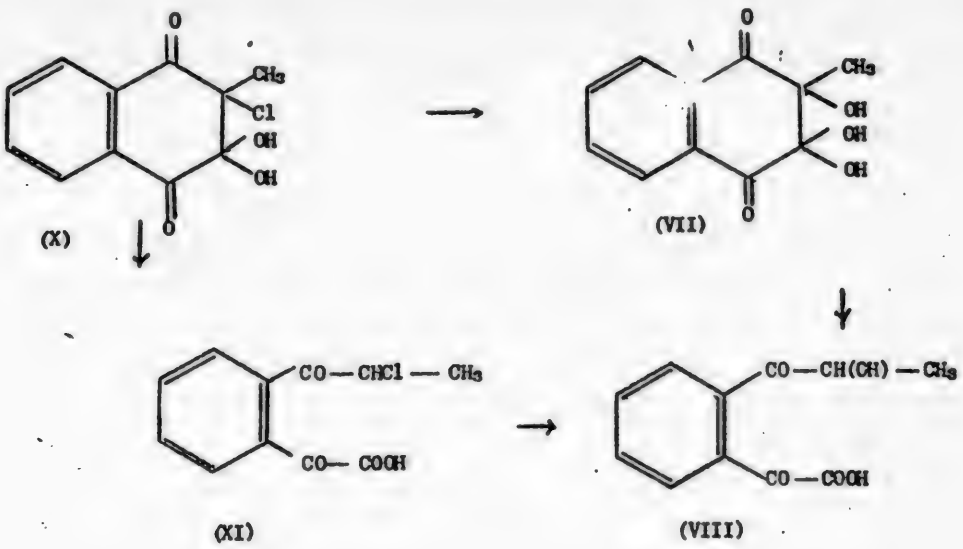
It was soon found, however, that only 10% of acid (XI) can be converted to acid (VIII), even after 10 hours of boiling with water. It followed that the assumption expressed is evidently incorrect and that acid (VIII), some 30% of which is formed in the first case, is formed in full in hardly 45 minutes, via acid (XI). On the other hand, it was discovered that when compounds (X) and (XI) are boiled with water, the following relationship prevails between duration of boiling and the amount of chlorine liberated, as determined in the solution by titration with silver nitrate (Table 1).

The figures in this table very clearly indicate that the assumption made above is wrong. It is quite clear that most of acid (VIII), the genesis of which is linked with the liberation of the halogen, cannot be formed via acid (XI). In fact, when compound (X) is boiled with water, some 50% is liberated after no more than 20 minutes, whereas with acid (XI) only 10% of chlorine can be found after 10 hours. Hence, the bulk of acid (VIII) is formed in some other manner, only a minor portion being produced via acid (XI).

TABLE 1

| Duration of boiling (min) | Amount of chlorine liberated (%) | |
|---|---|---|
| | Compound (X) | Compound (XI) |
| 1 | 10.47 | — |
| 5 | 34.89 | — |
| 10 | 44.43 | — |
| 20 | 48.37 | 6.55 |
| 120 | 50.10 | 8.16 |
| 600 | 53.80 | 10.28 |

Clarification of these circumstances led us to conclude that under the given conditions the hydrolytic cleavage of compound (X) to acid (XI) is paralleled by another process, viz.: to begin with, replacement of the halogen atom in compound (X) by hydroxyl, resulting in the formation of the corresponding hydrated hydroxytriketone (VII), which is then converted into acid (VIII) as a result of the subsequent hydrolytic cleavage of the ring groupings. Thus the formation of the end compounds (XI) and (VIII) must proceed as follows:

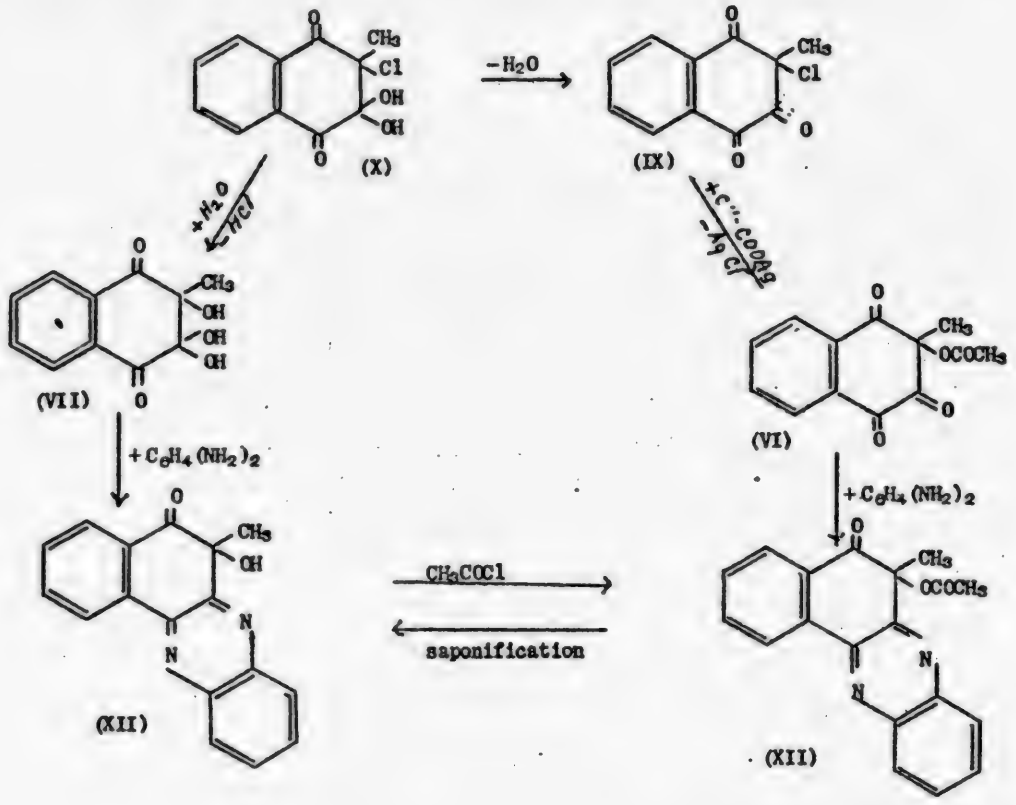



The correctness of the proposed diagram might be easily demonstrated if we were able to isolate the hydrated hydroxytriketone (VII), either as such, or as one of its derivatives, then proving that it actually can be transformed into the acid (VIII) by heating with water.

It developed that it was actually possible to demonstrate the presence of the hydroxytriketone (VII) among the reaction products when all the given conditions were observed; it was isolated from an aqueous solution as its quinoxaline derivative that was practically insoluble in water. After recrystallization from alcohol and benzene, the latter was obtained in pure form, having a m.p. of 189°. Its analysis data conformed with Formula (XII). The yield was about 15%, in terms of the initial compound (X). Acetylation of the isolated quinoxaline derivative with acetyl chloride in pyridine yielded the corresponding acetyl derivative with a m.p. of 213-214°, whose analytical data fitted Formula (XIII).

To confirm the structure of the compounds we had synthesized and to search for other ways of preparing the hydroxytriketones that interested us, we undertook at the same time an endeavor to replace the halogen atom in the chlorotriketone (IX) by an acetoxy group. This reaction can be easily effected by heating the freshly distilled chlorotriketone (IX) for three minutes with silver acetate at 145-155°. The acetoxytriketone (VI) is obtained in pure form without difficulty, its yield being 80%. This reaction cannot be performed with the hydrated form of the chlorotriketone (X), as the split-off water decomposes the acetoxytriketone formed.

The acetoxytriketone synthesized by us crystallizes easily from benzene. It is prepared in unhydrated form and has a m.p of 147°. Its analytical data conform with formula (VI). Ethyl acetate is formed when it is heated with alcohol in the presence of sulfuric acid. When boiled in a benzene solution with ortho phenylene diamine, the acetoxytriketone is converted into the quinoxaline derivative with a m.p. of 213-214°. This substance proved to be identical with compound (XIII), which we had previously prepared by acetylation of the quinoxaline derivative of the hydroxytriketone (XII). On the other hand, boiling the substance with a m.p. of 213-214° in an alcohol solution in the presence of hydrochloric acid causes it to saponify, the quinoxaline derivative of the hydroxytriketone with a m.p. of 189° being formed. This latter is identical with the compound we had already synthesized from the hydrated hydroxytriketone (VII) and ortho phenylene diamine. All the transformations effected by us may be grouped in an overall diagram as shown below:




The cycle of transformations described above leaves no room for doubt as to the structure of the hydrated hydroxytriketone (VII) or of the acetoxytriketone (VI). Nor is there any doubt about the genesis of the hydrated hydroxytriketone (VII) via the conversion of compound (X) into ortho lactyl-phenyl-glyoxylic acid (VIII) by boiling with water. The latter circumstance is further supported by the results of an investigation into the conditions governing the hydrolytic cleavage of the hydrated hydroxytriketone (VII). It was shown that it is completely converted into the acid (VIII) by 40–45 minutes of boiling with water. In the presence of alkali this process takes place practically instantaneously even in the cold. As for the acetoxytriketone (VI), its conversion into the acid (VIII) proceeds more slowly owing to the presence of the acetylated hydroxyl, requiring 3–4 hours of boiling with water.

## EXPERIMENTAL*

### I. Method of Preparation and Properties of 2-Methyl-1,2,3,4-Tetrahydronaphthalene--01-2-Trione-3,4 (V)

1. Behavior of 2-chloro-2-methyl-1,2,3,4-naphthalenediol-3,3-dione-1,4 (X) and ortho (α-chloropropionyl)-phenyl-glyoxylic acid (XI) when boiled with water.**

A weighed portion of the substance under investigation is placed in 20 ml of water, rapidly heated to the boiling point, and the solution kept at the boil for a definite period of time in a flask fitted with a reflux condenser. After cooling the number of chlorine ions in the solution is determined by the Volhard method.

* The analytical part of the research was carried out with the assistance of E.A. Ignatyeva, to whom we wish to express our appreciation.

** The preparation of these compounds was described in Paper VII [5].

The results of the experiment are listed in Table 2.

TABLE 2

| Duration of boiling | Batch weight (g) | N/10 $AgNO_3$ (ml) | | Chlorine found % |
|---|---|---|---|---|
| | | Found | Computed | |
| (min) | | Compound (X) | | |
| 1 | 0.1768 | 0.77 | 7.35 | 10.47 |
| 5 | 0.1751 | 2.54 | 7.28 | 34.89 |
| 10 | 0.1403 | 2.59 | 5.83 | 44.43 |
| 20 | 0.1556 | 3.13 | 6.47 | 48.37 |
| 120 | 0.1254 | 2.61 | 5.21 | 50.10 |
| 600 | 0.1770 | 3.96 | 7.36 | 53.80 |
| | | Compound (XI) | | |
| 20 | 0.1696 | 0.43 | 6.56 | 6.55 |
| 120 | 0.1343 | 0.43 | 5.27 | 8.16 |
| 600 | 0.1742 | 0.69 | 6.74 | 10.28 |

2. Quinoxaline derivative of the hydroxytriketone (XII).

a) Preparation. 200 ml of water and 10 g of the hydrated chlorotriketone (X) are boiled together for 15 minutes in a flask fitted with a reflux condenser. After the solution has cooled, it is filtered to free it of the slight quantity of light-yellow tarry substance that separated out, and the filtrate is then extracted three times with ether, 50 ml of ether being used each time*.

After the ether is driven off in vacuum without the application of heat, a solution of 1 g of ortho phenylene diamine in 40 ml of water is added to the cold solution. A white crystalline deposit soon settles out; it is filtered out, washed with water, 10% sulfuric acid, and then water again, after which it is dried in air. The weight of the quinoxaline derivative prepared is 1.75 g (yield: 15.2%). Recrystallization from ethyl alcohol and then from benzene yields a white crystalline substance with a m.p. of 188–189°, which turns yellow upon exposure to light.

$C_{17}H_{12}O_2N_2$. Found %: C 73.81; H 4.17. Calculated %: C 73.91; H 4.35.

b) Acetylation. 0.2 g of the substance is dissolved in 2 ml of pyridine and, after 2 ml of acetyl chloride has been added, the flask is closed with a stopper fitted with a wide and long outlet tube. A violent reaction soon sets in, accompanied by intense heating of the reaction mass. The contents of the flask are cooled off and then treated several times with 10% sulfuric acid. The tarry substance left behind is carefully washed with water and then triturated with 1 ml of alcohol. The tar dissolves in the alcohol, whereas the acetylation product formed in the reaction, which is only slightly soluble in cold alcohol, is filtered out and washed with a small quantity of alcohol. 0.15 g of a white crystalline substance is obtained; after double recrystallization from alcohol it fuses at 213–214°, and causes no depression of the melting point when mixed with the quinoxaline derivative of the acetoxytriketone (m.p.: 214°), described in Experiment II, 2.

3. Hydrolytic Cleavage of the hydroxytriketone (V).

a) 1 g of the hydrated chlorotriketone (X) is placed in 20 ml of water and then boiled for 10 minutes. After cooling the solution is extracted with ether three times, and the ether dis-

* 5 g of ortho (α-chloropropionyl)-phenyl-glyoxylic acid, with a m.p. of 95° (from dichloroethane), was isolated from the ether solution. Its properties are described in detail in Paper VII [5].

solved in the aqueous solution is expelled in vacuum without the application of heat. The 20 ml of solution obtained contained 0.15 g of the hydroxytriketone, which was subjected to hydrolytic cleavage without preliminary isolation. The amount of the hydroxytriketone in the solution before the beginning of the experiment and during the run was determined by the amount of the quinoxaline derivative formed when an aqueous solution of ortho phenylene diamine is added. It was found that after no more than 20 minutes of boiling a considerable proportion of the hydroxytriketone underwent hydrolytic cleavage: after 30 minutes only an insignificant amount of it was left, while after 45 minutes all of it was decomposed — no more of the quinoxaline derivative of the hydroxytriketone settled out when a solution of ortho phenylene diamine was added.

The hydrolytic cleavage of the hydroxytriketone under these conditions results in the formation of ortho lactyl-phenyl-glyoxylic acid, which can be isolated as described in Paper VII [5].

b) The solution of the hydroxytriketone in water was prepared as described in the previous experiment. 1 g of the hydrated chlorotriketone was used to make up 20 ml of an aqueous solution, containing 0.15 g of the hydroxytriketone as determined by the quantity of the quinoxaline derivative formed. An equal quantity of a caustic soda solution was added to 10 ml of the foregoing solution in order to make the concentration of alkali in the solution equal 1%. After 30 seconds the alkaline solution was acidified with sulfuric acid, and then an aqueous solution of ortho phenylene diamine was added to it. No deposit of the quinoxaline derivative was formed, all the hydroxytriketone undergoing hydrolytic cleavage. Ortho lactyl-phenyl-glyoxylic acid could be isolated from the solution (cf. the foregoing experiment).

## II. Preparation and Properties of the Acetylated 2-Methyl-1,2,3,4-Tetrahydronaphthalene-ol-2-Trione-1,3,4 (VI)

1. Preparation of the acetoxytriketone (VI). 2 g of the hydrated chlorotriketone (X) is placed in a 5-ml Cluizen flask and dehydrated under the conditions set forth in Paper VII [5], the chlorotriketone (IX) being formed by distillation. The latter is collected in a receiver that consists of a small test tube fitted with an outlet tube at the side. When distillation is complete, the test tube containing the chlorotriketone is quickly disconnected and stoppered, while the side outlet is connected to a calcium-chloride tube. The chlorotriketone obtained weighs 1.6 g. Yield: 86.5%.

To eliminate any traces of moisture the chlorotriketone thus prepared is then heated over an oil bath for 5 minutes at 150°, after which 3 g of silver acetate, previously dried in vacuum at 50-60°, is added to the hot mobile oil. The opening of the test tube is closed by a stopper fitted with a glass rod, required for stirring the reaction mass. The reaction mass is heated for 3 minutes* over an oil bath at a bath temperature of 145-155°. After cooling the solidified mass is pulverized in a mortar, and the acetoxytriketone (VI) formed is repeatedly extracted in the cold with ether, about 200 ml of the latter being required. Animal charcoal is added to the ether solution and then filtered out 3-4 hours later, after which the ether is driven off to dryness. There remain 1.7 g of a yellow crystalline substance with a m.p. of 140-142°. Recrystallization from 3 ml of benzene yields 1.4 g of the acetoxytriketone with a m.p. of 147°. Yield: 78%, in terms of the chlorotriketone.** The substance is easily soluble in chloroform, acetone, heptane, and methyl acetate.

When the acetoxytriketone is heated with ethyl alcohol and a small quantity of sulfuric acid, ethyl acetate is formed which bears out the presence of an acetoxy group in the molecule.

| | | |
|---|---|---|
| | Found %: | C 63.58; H 3.96. |
| $C_{13}H_{10}O_5$. | Calculated %: | C 63.41; H 4.06. |

* Longer heating is undesirable as it results in considerable tarring of the reaction product.

** The acetoxytriketone (VI) can also be prepared by the action of anhydrous potassium acetate upon the chlorotriketone (IX), but this method gives a considerably lower yield.

2. Quinoxaline derivative of the acetoxytriketone (XIII).

a) Preparation. 0.5 g of the acetoxytriketone (VI) is dissolved in 2 ml of benzene and 0.3 g of ortho phenylene diamine, dissolved (with heating) in 2 ml of benzene, are added to the hot solution. After boiling for 3 minutes the reaction mass is cooled, and the precipitate that settles is filtered out. Weight: 0.7 g. The substance obtained is fairly soluble in benzene and hardly so in alcohol. After recrystallization from alcohol and then from a small quantity of benzene, we obtain a white crystalline substance with a m.p. of 213– 214°.

| | | | |
|---|---|---|---|
| | Found %: | C 71.53; | H 4.58. |
| $C_{19}H_{14}O_3N_2$. | Calculated %: | C 71.69; | H 4.40. |

b) Saponification. Into a round-bottomed flask there are put 0.1 g of the quinoxaline derivative of the acetoxytriketone prepared in the foregoing experiment, 10 ml of ethyl alcohol, and 10 ml of concentrated hydrochloric acid. The mixture is boiled with a reflux condenser for 30 minutes. The cooled brown solution is poured into 300 ml of water. A few hours later a deposit settles out; this is filtered washed with water, and air-dried. Weight: 0.1 g. After recrystallization from 3 ml of alcohol the substance fuses at 137° and causes no depression of the melting point when mixed with the quinoxaline derivative of the hydroxytriketone prepared in Experiment I, 2a.

3. Hydrolytic cleavage of the acetoxytriketone (VI).

a) 0,5 g of the acetoxytriketone is boiled for 30 minutes with 5 ml of water; the substance being observed to have fully dissolved after 20 minutes have elapsed. Upon cooling an extremely small quantity of a yellow precipitate, with a m.p. of 196–198°, settles out. The aqueous solution is extracted with ether three times, after which the ether is driven off to dryness in vacuum. We obtain 0.04 g of a white crystalline substance with a m.p. of 226–228°, which fuses at 232° (decomp.) after recrystallization from water and produces no depression of the melting point when mixed with the ortho lactyl-phenyl-glyoxylic acid described in Paper IV [4].

The ether solution obtained above is dried with sodium sulfate, and the ether is driven off. There remains 0.45 g of a light-yellow non-crystallizing oil. When this oil is boiled with water for 3 hours, it is converted into ortho lactyl-phenyl-glyoxylic acid, which may be isolated as described above.

b) 0.3 g of the acetoxytriketone is boiled with 3 ml of water for 3 hours. When the solution is cooled, the minute deposit that settles is filtered out. M.p.: 196–198°. After the precipitate is filtered out, the solution is extracted with ether. The ether solution is dried with sodium sulfate, and the ether is driven off. There remains behind 0.16 g of an oil, part of which crystallizes by heating to 100° at 5 mm, after the traces of ether and acetic acid are eliminated. There is left 0.1 g of ortho lactyl-phenyl-glyoxylic acid with a m.p. of 226–227°. The m.p. after recrystallization from water is 232° (decomp.).

After the ether extraction the water is driven off from the aqueous solution to dryness in vacuum. We obtain 0.12 g of ortho lactyl-phenyl-glyoxylic acid with a m.p. of 226–227°. The m.p. after recrystallization from water is 232° (decomp.). Yield: 81.5%.

4. Conversion of the acetoxytriketone (VI) into 2 hydroxy-1,4-naphthoquinone. 0.2 g of the acetoxytriketone and 20 ml of a 5% aqueous solution of caustic soda are put into a two-necked bottle fitted with a reflux condenser and a tube reaching down to the bottom of the flask, through which air is passed during the experiment. The colorless solution produced is boiled for 30 minutes. One to two minutes after boiling begins the solution turns red. The cooled solution is acidulated with 10% sulfuric acid, causing a yellow precipitate to settle out. The solution and the precipitate are extracted with ether. The ether solution is dried with sodium sulfate, and the ether is driven off. There remains 0.1 g of yellow crystals, which are twice recrystallized from methyl alcohol. M.p.: 191°. A sample of the substance mixed with 2-hydroxy-1,4-naphthaquinone fuses at the same temperature.

## CONCLUSIONS

In order to investigate the conditions and the nature of the hydrolytic cleavage of the hydroxytriketones of the tetrahydronaphthalene series, methods of preparation have been developed

and the synthesis of 2-methyl-1,2,3,4-tetrahydronaphthalene-ol-2-trione-1,3,4 has been effected. The second of the methods developed makes it possible to synthesize the acetyl derivative of this hydroxytriketone.

It has been shown that these compounds undergo hydrolytic cleavage to ortho lactyl-phenyl-glyoxalic acid very easily upon heating with water, as well as in the cold when acted upon by aqueous solutions of alkalis.

Comparison of these results with the conditions for the cleavage of 2-methyl-1,4,-naphthoquinone, the oxide of 2-methyl-1,4-naphthoquinone, and 2-methyl-3-hydroxy-1,4-naphthoquinone leads to the conclusion that the following statement holds true for the series of compounds investigated: the higher the degree of oxidation of the original quinone molecule, the easier the hydrolytic cleavage.

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* (Consultants Bureau English Translation, p. 165-173. Article G-25.)
** (Consultants Bureau English Translation, p. 175-180. Article G-26.)
***(Consultants Bureau English Translation, p. 447 ff).

# OXIDATIVE AND OXIDATIVE-HYDROLYTIC TRANSFORMATIONS OF ORGANIC MOLECULES

## IX. STUDY OF THE METHODS OF TRANSFORMING ORTHO (α-CHLOROPROPIONYL)-PHENYL-GLYOXYLIC ACID INTO CARBOXYLIC COMPOUNDS

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It is known that in the oxidative-hydrolytic and purely hydrolytic cleavage of some quinones and cyclic polyketones, products are formed as intermediates in which the ring grouping is already opened and which are able to re-form ring systems under certain conditions. These reactions most often depend upon the processes of intramolecular condensation, which are at times accompanied by a number of subsidiary transformations. A rather large number of examples of this type is reported in the literature, in most instances the formation of five-membered rings having been observed, with six-membered rings much less frequent.* But not a single mention is found of the simultaneous formation of both five- and six-membered rings from the same intermediate alicyclic compound. But it was precisely an instance of this sort that we encountered in our study of the properties of some of the products of the cleavage of triketones of the tetrahydronaphthalene series described by us previously [5]. On the other hand, we had come across cases in which a five-membered ring was formed in circumstances that are rather unusual for this type of conversion. As these examples might possess a certain interest in all problems of the hydrolytic and oxidative-hydrolytic cleavage of the quinones, thus affording insight into the further fate of the initial products of the molecule's cleavage, we subjected them to detailed investigation. A description of the results obtained is the subject of the present paper.

It was found that the chlorotriketone (I), its hydrated form (II), and ortho (α-chloropropionyl)-phenyl-glyoxylic acid (III)** all undergo the same transformation upon heating with aqueous solutions of alkalis in a stream of air for a short time, splitting off one molecule of $CO_2$ and finally ending up with 2-hydroxy-1,4-naphthoquinone (IV) and 2-methyl-indandione-1,3 ( V).

Both of these compounds have been described in the literature, and the elucidation of their structure therefore presented no great difficulties. The first one was identified by its melting point as well as in the form of the corresponding anilide and 2-hydroxy-3-nitro-1,4-naphthoquinone, the properties of which corresponded to the data in the literature [6,7]. The second compound — 2-methyl-indandione-1,3 (V) — was identified by the melting point and as the 2-bromo derivative of the phenylhydrazone; their properties coincided with those described in the literature [8]. Moreover, we obtained the semicarbazone and the para nitrobenzylic ether of the enolic form of compound (V); the analysis of the latter two also confirmed the structure of the 2-methyl-indandione-1,3 prepared by us.

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* For the literature on this problem, cf. Paper I [1]. Cf. also Papers II [2], IV [3], and VI [4].

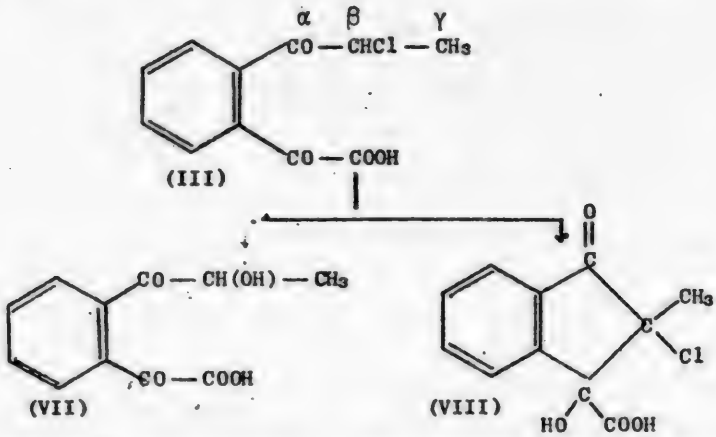
**The preparation of these compounds and their properties are set forth at length in Paper VII [5].

Compounds (I), (II), and (III) behave somewhat differently when heated with aqueous solutions of alkalis and no atmospheric oxygen present (in an atmosphere of hydrogen). In all of these cases 1,2-naphthohydroquinone-4-carboxylic acid (VI) is formed instead of 2-hydroxy-1,4-naphthoquinone (IV). As for 2-methyl-indandione-1,3, it is obtained in almost the same quantities, as in the experiments performed in the presence of atmospheric oxygen. The splitting off of carbon dioxide likewise takes place, but it is formed in smaller quantities. The diminution in its yield corresponds to the quantity of acid (VI) produced.

The 1,2-naphthohydroquinone-4-carboxylic acid (VI) prepared by us has already been described in the literature [3, 9]. Its melting point identified it with a preparation synthesized by another method: from ortho lactyl-phenyl-glyoxylic acid (cf. Paper IV [3]). Moreover, oxidation by nitric acid converted it into 1,2-naphthoquinone-4-carboxylic acid, the properties of which coincided with those described in the literature [3, 9]. Thus, all the described properties of the final compounds isolated by us leave no room for doubt as to their structure. The method of preparation is shown in the diagram on p. 459.

Some of the intermediate stages of this diagram must be considered at greater length. The first stages of these transformations are fairly obvious. In fact, we demonstrated in Paper VII [5] that compound (I) converts into compound (II) with extreme ease, even upon mere contact with water, whereas compound (II) is converted into compound (III) almost instantaneously in the cold when acted upon by aqueous solutions of alkalis. Acid (III), however, forms the end compounds (V) and (IV) or (VI) fairly rapidly only when boiled with an alkaline solution. This makes it apparent that acid (III) must be formed as an intermediate product during the conversion of compounds (I) and (II) to 2-methyl-indandione-1,3 (V) and 2-hydroxy-1,4-naphthoquinone (IV) or 1,2-naphthohydroquinone-4-carboxylic acid (VI).

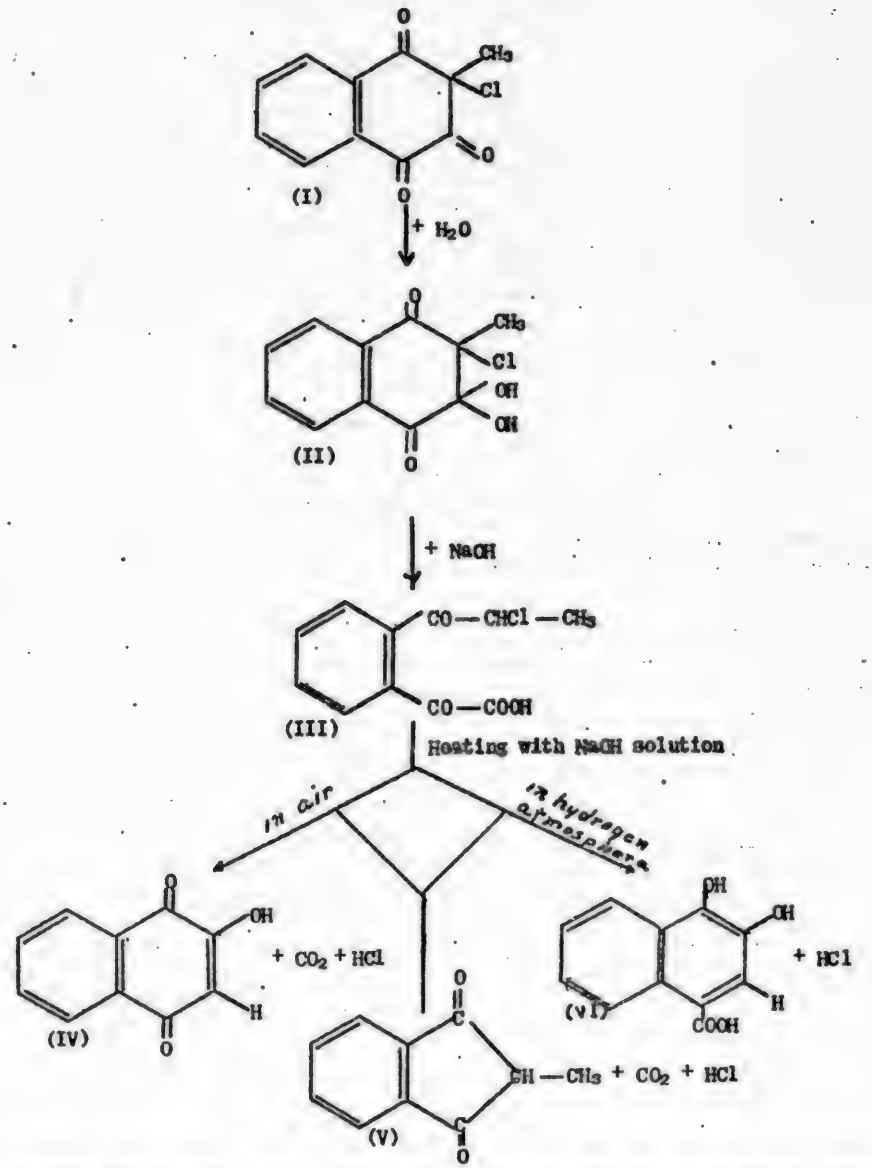
As for the further steps of the transformations, they are much more complicated. As will be shown below, two different directions of the process compete with each other here. On the one hand, the halogen atom in acid (III) is replaced by hydroxyl under the influence of the aqueous alkaline solution, which first results in the formation of ortho lactyl-phenyl-glyoxylic acid (VII). On the other hand, owing to the considerable mobility of the hydrogen atom attached to the β-carbon atom of acid (III), the latter may also undergo other changes, being converted in this first stage to the cyclic α-hydroxy acid (VIII).




Both of these compounds are formed simultaneously, immediately undergoing subsequent transformations that proceed parallel with and independent of one another.

The intermediate formation of ortho lactyl-phenyl-glyoxylic acid (VII) is apparent to some extent. In fact, it was demonstrated in Paper IV [3] that this acid is easily cyclized when heated

with aqueous alkaline solutions in the presence of atmospheric oxygen, splitting off a molecule of carbon dioxide and forming 2-hydroxy-1,4-naphthoquinone (IV), whereas in a hydrogen atmosphere it is converted to 1,2-naphthohydroquinone-4-carboxylic acid (VI), which cannot be decarb-




oxylated under these conditions. Thus, the same compounds that we isolated by the action of an alkaline solution on acid (III) are here formed as end products in both cases as well.

It is quite essential to emphasize at this point that the behavior of both acids [(III) and (IV)] is the same when these reactions are carried out in air or in a hydrogen atmosphere. On the other hand, it must be borne in mind that when we boil acid (III) with an alkaline solution in a hydrogen atmosphere, we observe that the quantity of carbon dioxide formed is diminished, it being formed in the same degree, as it happens, as the 1,2-naphthohydroquinone-4-carboxylic acid (V) isolated by us; the formation of the latter not being accompanied by the liberation of

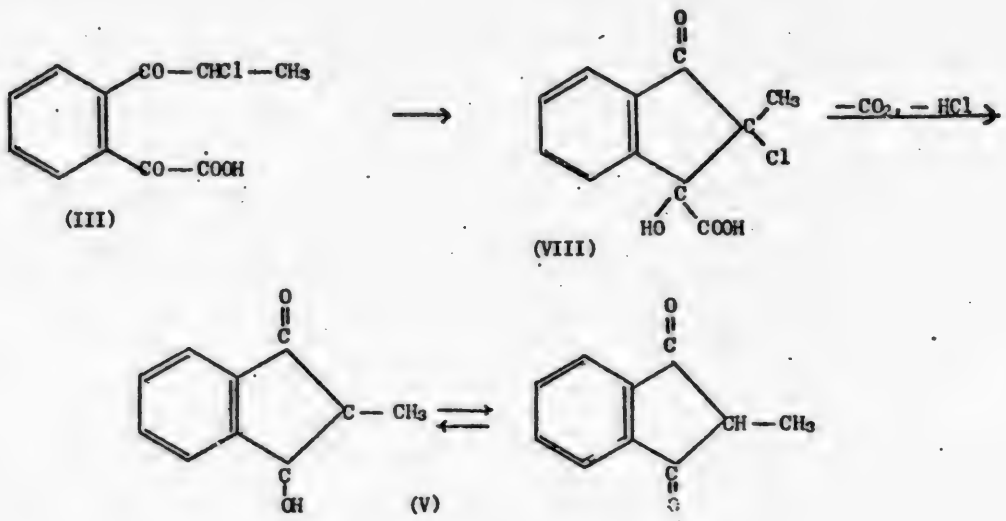
carbon dioxide. Hence, we have every reason to assume that the conversions of acid (III) to 2-hydroxy-1,4-naphthoquinone (IV) or to acid (VI) are linked to the intermediate formation of ortho lactyl-phenyl-glyoxylic acid (VII). The mechanism of the conversion of this acid into compounds (IV) and (VI) were investigated at length earlier (cf. Paper IV [3]).

Thus the path leading to the genesis of these end products becomes clear.

Let us examine the possible ways of converting acid (III) into 2-methyl-indandione-1,3 (V).

These transformations can not take place via ortho lactyl-phenyl-glyoxylic acid (VII), since the latter does not convert into compound (V) when boiled with an aqueous alkaline solution, whether atmospheric oxygen is present or not. Hence, the five-membered ring must be formed in the acid (III) itself. There is yet another factor operating in this direction. Owing to the fact that the β-carbon atom in the molecule of acid (III) is attached to the carbonyl group as well as to the halogen atom, the hydrogen atom attached to this carbon atom must possess very high mobility. This latter circumstance is of basic importance for the marked facility with which intramolecular condensations of this kind take place (for details cf. Paper I [1]). In the first stage this process should result in the formation of the hydroxy acid (VIII). There is a fairly large number of analogies in the literature. At times these hydroxy acids can be isolated as such; more often they undergo some further transformation at the very instant of their formation, in particular, decarboxylation.*

In the present case this intermediate hydroxy acid (VIII) cannot be isolated either, since it immediately undergoes decarboxylation, simultaneously liberating hydrogen chloride and being transformed into the terminal 2-methyl-indandione-1,3 (V). The formation of carbon dioxide during the formation of compound (V) was observed by us when this process was carried out in the presence of atmospheric oxygen as well as in a hydrogen atmosphere. Hence, the conversion of acid (III) to 2-methyl-indandione-1,3 (V) may be represented by the following diagram:




A curious circumstance should be noted at this point. It was emphasized in Paper IV [3] that the conversion of acid (VII) to 2-hydroxy-1,4-naphthoquinone (IV) necessitates the presence of oxygen, since the six-membered α-hydroxy acid that is formed as an intermediate product can undergo solely an oxidative decarboxylation. Yet, according to our data, acid (III) can be converted into 2-methyl-indandione-1,3 (V) in a hydrogen atmosphere as well.

* Cf. Paper I [1] for exhaustive literature references on this point.

Hence, the intermediate five-membered α-hydroxy acid (VIII) can undergo hydrolytic decarboxylation but not an oxidative one.

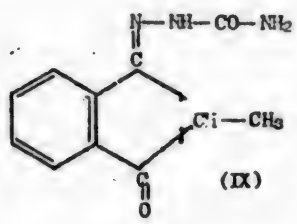
These transformations are of interest because they indicate with sufficient vividness how complex and varied may be the secondary reaction that initial compounds formed as the result of hydrolytic or oxidative-hydrolytic cleavage of quinones and cyclic polyketones can undergo. Owing to the ability of ortho(α-chloropropionyl)-phenyl-glyoxylic acid (III) to convert into ortho lactyl-phenyl-glyoxylic acid (VII) at the same time as into the cyclic α-hydroxy acid (VIII), we here have the rare opportunity of simultaneously forming new five- and six-membered ring groupings.

Another instance of analogical conversions investigated by us and dealt with below is of interest in another connection. It demonstrates how easily the reactions that result in the formation of new cyclic compounds may sometimes occur.

In an endeavor to obtain the ortho(α-chloropropionyl)-phenyl-glyoxylic acid (III) in the form of its semicarbazone we discovered that this acid is gradually converted into a semicarbazone of 2-methyl-indandione-1,3 (IX) when treated in alkaline solution with an equivalent quantity of potassium acetate in the cold and in the presence of semicarbazide hydrochloride. During a twenty-four hour period the reaction is 50% complete; it involves the splitting off of one molecule of carbon dioxide. Its course is unaffected by the presence or absence of atmospheric oxygen. The nature of the process is very similar to the above-described conversion of ortho (α-chloropropionyl)-phenyl-glyoxylic acid (III) when heated in an alkaline solution, but it differs from it in not at all resulting in the formation of 2-hydroxy-1,4-naphthoquinone (IV) or 1,2-naphthohydroquinone-4-carboxylic acid (VI) or any of their derivatives.

The reason for their not being present among the end products of the reaction is apparently linked up with the fact that here we do not have the conditions that favor the formation of acid (VII) as well as its subsequent transformations, which occur with ease only in an alkaline medium. Here only one of the two alternative courses described above is possible, it developing, moreover, that it can proceed under remarkably mild conditions.

The semicarbazone isolated by us was identified by its melting point and properties as the semicarbazone (IX) prepared directly from 2-methyl-indandione-1,3 (V). Its analytical data likewise fit Formula (IX):



(IX)

Comparison of these results with those we obtained in our study of the transformations of ortho (α-chloropropionyl)-phenyl-glyoxylic acid (III) in an alkaline solution again corroborates the correctness of the reaction diagrams set forth above.

## EXPERIMENTAL *

1. Transformations of 2-chloro-2-methyl-1,2,3,4-tetrahydronaphthalene-diol-3,3-dione-1,4 (II) in an alkaline medium and in an atmosphere of air. a) 1. g of the substance is dissolved in 30 ml of a 5% solution of caustic soda and boiled for 15 minutes in a flask with a reflux condenser, a current of air that has been freed from carbon dioxide being passed through the solution uninterruptedly. The solution, which turns pale red even when cold, takes on a cherry-red color when it is boiled. The cooled solution is acidulated with 10% sulfuric acid; the precipitate formed is filtered out, washed with water, and dried in air. Weight: 0.53 g.

This precipitate is a mixture of two substances: 2-hydroxy-1,4-naphthoquinone (IV) and 2-methyl-indandione-1,4 (V), which are separated by taking advantage of their differing solubilities in benzene. The precipitate is carefully triturated in the cold with 20 ml of benzene, the undissolved part of the precipitate being filtered out and washed twice with benzene. The benzene solution is boiled with animal charcoal, and then the benzene is driven off. The residue

* The analytical portion of the research was done with the assistance of E.A. Ignatyeva, to whom we express our deep appreciation.

weighs 0.35 g. M.p.: 65-80°. Two recrystallizations from a small quantity of ethyl alcohol, using animal charcoal, enables us to obtain a white crystalline substance with a m.p. of 86°, which is the 2-methyl-indandione-1,3 described in the literature [8]. Yield 23.5%.

Found %: C 75.21; H 5.25.
$C_{10}H_8O_2$. Calculated %: C 75.00 H 5.00.

The light-yellow crystalline substance that did not dissolve in the benzene has a m.p. of 150-170°. Weight: 0.15 g. After recrystallization from benzene the m.p. is 190-191° (decomp.); this substance is 2-hydroxy-1,4-naphthoquinone. Yield: 21%.

The compounds isolated were further identified by several of their derivatives. The 2-hydroxy-1,4-naphthoquinone was heated with aniline in glacial acetic acid to produce the corresponding anilide with a m.p. of 192° (from glacial acetic acid), and nitrated with nitric acid to produce 2-hydroxy-3-nitro-1,4-naphthoquinone with a m.p. of 158° [6,7].

The 2-methyl-indandione-1,3 was obtained as a phenyl-hydrazine with a m.p. of 162-164° (from alcohol) and as 2-methyl-bromoindandione-1,3 with a m.p. of 90-91°. The latter compound was prepated by bromination when heated in an acetic-acid medium [8]. The properties of all the derivatives prepared corresponded with the data in the literature.

Moreover, a new derivative of 2-methyl-indandione-1,3: its para nitrobenzyl ester. The latter was prepared as follows: 0.1 g of the substance was dissolved in 3 ml of 65% ethyl alcohol. To the solution there was added 0.04 g of caustic soda in 1.5 ml of 65% alcohol, and then a solution of 0.16 g of para nitrobenzyl bromide in 3 ml of alcohol of the same strength. The mixture was boiled for 1 hour and then evaporated in vacuum at 25° to reduce its volume. The precipitate formed was filtered out, washed with water, and twice recrystallized from ethyl alcohol. M.p.: 120-121°. Weight: 0.15 g. Yield: 82%.

Found %: C 69.07; H 4.64; N 4.69.
$C_{17}H_{13}O_4N$. Calculated %: C 69.12; H 4.41; N 4.74.

b) Determination of the carbon dioxide formed. Determination of the carbon dioxide liberated when the hydrated chloro-triketone (II) is converted into 2-methyl-indandione-1,3 and 2-hydroxy-1,4-naphthoquinone is effected in a three-necked flask, fitted with a reflux condenser, a dropping funnel, and a tube reaching down to the bottom of the flask through which air was introduced. The latter was first freed of its carbon dioxide by passing it through a 40% solution of caustic soda. The air passed out of the system, together with the carbon dioxide formed as a result of the reaction, through an opening in the condenser; it then passed through a titrating solution of alkali contained in two flasks connected together in series. The system terminated in a Tishchenko bottle filled with a 40% solution of caustic soda. 0.1566 g of the substance was placed in a three-necked flask. 30 ml of a N/10 solution of alkali was poured into each flask to absorb the carbon dioxide. After the airtightness of the system had been checked, air was allowed to pass through; the air must pass through the system throughout the experiment. Then, allowing 40 ml of a 5% solution of caustic potash to enter the reaction flask from the dropping funnel, we boiled the whole solution for 30 minutes. The solution was then cooled and acidulated with 30% sulfuric acid, which was introduced through the same dropping funnel. After this, the solution was again heated to boiling and boiled for 15 minutes to remove completely the carbon dioxide formed. After the end of the run, the alkaline solution that served to absorb the carbon dioxide was titrated back with N/10 acid solution, first with phenolphthalein and then with methyl orange. The carbon dioxide liberated consumed 9.32 ml of N/10 alkaline solution. It was found in a preliminary test that the carbon dioxide obtained from the potash contained in the 40 ml of a 5% solution of caustic potash used for the reaction used up 3.24 ml of N/10 alkaline solution. Hence, the carbon dioxide formed in the reaction used up 6.08 ml of N/10 alkaline solution, whereas 6.50 ml should have been consumed according to computations. Thus the yield of alkali was 93.4%.

2. Transformations of ortho (α-chloropropionyl)-phenyl-glyoxylic acid (III) in an alkaline medium and in an atmosphere of air. 1.5 g of the substance and 40 ml of a 5% aqueous solution of caustic soda were boiled together for 15 minutes under the same conditions as Experiment 1 a.

The mixture, consisting of 2-methyl-indandione-1,3 and 2-hydroxy-1,4-naphthoquinone, that precipitated out when the alkaline solution was acidulated with 10% sulfuric acid was separated as in the previous Experiment 1a. We obtained 0.4 g of 2-methyl-indandione-1,3 with a m.p. of 86° (from alcohol). Yield: 27%. We also obtained 0.2 g of 2-hydroxy-1,4-naphthoquinone. M.p.: 190-191°, with decomposition (from benzene). Yield: 20%.

3. Transformations of 2-chloro-2-methyl-1,2,3,4-tetrahydronaphthalene-diol-3,3-dione-1,4 (II) in an alkaline medium and in a hydrogen atmosphere. The experiment is carried out in a small three-necked flask, equipped with a reflux condenser, a dropping funnel, and a tube extending to the bottom of the flask, through which the hydrogen enters. The latter is purified by passing it through an alkaline solution of potassium permanganate and an alkaline solution of pyrogallol. The hydrogen is also passed over a bed of incandescent copper to remove the last traces of oxygen. A small safety bottle is placed ahead of the reaction flask; this bottle also serves as a bubble counter for the stream of gas. The hydrogen leaves the system through the reflux condenser, connected to a Tischenko bottle filled with an alkaline solution of pyrogallic.

7 g of the substance and 90 ml of water are placed in the flask. After the airtightness of the system has been checked, the hydrogen begins to displace the air in the system. To eliminate the air that is dissolved in the water, the contents of the flask are boiled in a stream of hydrogen for 30 minutes, then allowed to cool, and a solution of 25.7 g of caustic potash in 140 ml of water is introduced into the flask 1.5 hours after the hydrogen stream was turned on. The reaction mixture is boiled for 30 minutes. After the dark-red solution has cooled, with the stream of hydrogen still flowing, it is acidulated with 40 ml of 50% sulfuric acid, which is introduced through the dropping funnel.

As the solution is acidulated, a rapidly crystallizing oil settles out. The deposit is filtered out, washed with water, and dried in air. Weight 3.4 g. It consists of two substances: 2-methyl-indandione-1,3 (V) and 1,2-naphthohydroquinone-4-carboxylic acid (VI). Only the former is soluble in benzene. This property is employed to separate them by repeatedly boiling the deposit with benzene, using 20-25 ml of the latter each time.

The residue that is insoluble in benzene is pure 1,2-naphthohydroquinone-4-carboxylic acid, melting at 194-195° with decomposition. Weight: 1.3 g. Yield: 22%. The substance was found to be identical with a preparation of the same acid made under analogous conditions from ortho lactyl-phenyl-glyoxylic acid [3]. Moreover, the substance isolated was oxidized by nitric acid to 1,2-naphthoquinone-4-carboxylic acid, the properties of which corresponded to those described in the literature [9].

The benzene solution, prepared above, is dried with sodium sulfate, boiled with animal charcoal, and the benzene then driven off. The last traces of the latter are expelled in vacuum. What remains behind is a white crystalline substance, largely contaminated with a brown oil, which is removed with porous clay. There remains behind 1.1 g of a substance that fuses at 86° after crystallization from 2 ml of alcohol, animal charcoal being used. A sample, mixed with the 2-methyl-indandione-1,3 prepared in Experiment 1a, fused at the same temperature.

4. Transformations of ortho ($\alpha$-chloropropionyl)-phenyl-glyoxylic acid (III) in an alkaline medium and in a hydrogen atmosphere. a) The reaction and the isolation of the products obtained were effected under the conditions described for Experiment 3. 5 g of the substance was used. We obtained 1.5 g of 1,2-naphthohydroquinone-4-carboxylic acid with a m.p. of 194-195° (from water to which animal charcoal had been added). Yield: 37%. In addition, we isolated 0.3 g of 2-methyl-indandione-1,3 with a m.p. of 86° (from alcohol). Yield: 10%.

b) Determination of the carbon dioxide formed. The experiment was performed in a stream of hydrogen in the apparatus described in Experiment 3, supplemented by a Tishchenko bottle containing a 40% solution of caustic soda, inserted ahead of the three-necked bottle, and two flasks connected in series and containing a titrated alkaline solution, which served to absorb the carbon dioxide liberated during the reaction. These flasks were attached to the upper end of the condenser. The system was terminated with a Tishchenko bottle that was filled with a 40% solution of

caustic soda. Cf. Experiment 1b for the details of how the experiment was carried out. 0.3795 g of ortho (α-chloropropionyl)-phenyl-glyoxylic acid and 40 ml of water were placed in the reaction flask. After the system had been checked for airtightness, 25 ml of a 10% solution of caustic potash was introduced through the dropping funnel. 30 ml of a N/10 solution of caustic soda had previously been poured into each of the absorbing flasks. The air was driven out of the system by passing hydrogen through it for 2 hours. Then the alkaline solution is heated to the boiling point and boiled for 30 minutes. The cooled solution is acidulated with 25 ml of 30% sulfuric acid, which is introduced through the dropping funnel. Then the solution is boiled in a stream of hydrogen for 15 minutes to drive off the carbon dioxide formed, and, finally, the alkali serving as a carbon dioxide absorber is titrated back with N/10 acid solution, at first against phenolphthalein, and then against methyl orange.

13.63 ml of N/10 alkali solution was used up for the carbon dioxide liberated. It was determined in a preliminary test that 4.24 ml of N/10 alkali solution was required for the carbon dioxide obtained from the potash contained in the 25 ml of 10% caustic potash solution used for the reaction. Hence, the carbon dioxide liberated in the reaction used up 9.39 ml of N/10 alkali solution, whereas computation indicated that 14.86 ml should have been used. Hence, the yield was 63.9%.

5. Reaction of ortho (α-chloropropionyl)-phenyl-glyoxylic acid (III) with semicarbazide.

a) Preparation of the semicarbazone. 1.2 g of carefully pulverized acid is dissolved in the cold in 75 ml of water, 2.4 g of semicarbazide hydrochloride and 2.4 g of crystalline potassium acetate are added, and the colorless transparent solution is allowed to stand for 48 hours. A white precipitate begins to settle out of the solution within 4 hours, in the form of thin needles, the amount of which gradually increases. After 48 hours the deposit is filtered out, washed with water, and air-dried. Weight: 0.85 g. M.p.: 213° (decomp.). The substance crystallizes easily out of 50% acetic acid as well as out of alcohol. It dissolves slowly in a 5% solution of caustic soda in the cold and rapidly upon heating, forming an orange-red solution. When the alkaline solution is acidulated with 10% sulfuric acid the substance is reprecipitated unchanged. It fuses at 231° (decomp.) after triple recrystallization from alcohol.

| | | | | |
|---|---|---|---|---|
| | Found %: | C 61.02; | H 5.08; | N 19.16. |
| $C_{11}H_{11}O_2N_3$. | Calculated %: | C 60.83; | H 5.07; | N 19.35. |

The substance isolated proved to be identical in all its properties with the semicarbazone of 2-methyl-indandione-1,3 (cf. below, Experiment 6, for its preparation). A mixture of the two substances fuses with decomposition at 231°.

b) Determination of carbon dioxide. The determination of the carbon dioxide formed in the reaction of ortho (α-chloropropionyl)-phenyl-glyoxylic acid with semicarbazide is effected in a small two-necked flask, fitted with a reflux condenser and a tube extending down to the bottom of the flask, through which hydrogen enters. Ahead of the reaction flask and connected to it by a tube equipped with a stopcock there is placed a three-necked flask fitted with a reflux condenser, the upper end of which is connected to a Tishchenko bottle filled with an alkaline solution of pyrogallol. Tubes pass through the other two openings of this flask: the first, a short tube carrying the hydrogen, ends at the stopper itself; the second, a long tube that slides freely in the stopper, extends down to the bottom of the flask. The three-necked flask is intended for the preliminary boiling of the water in a hydrogen stream, which is required to remove the air and carbon dioxide dissolved in the water. The hydrogen is first passed through alkaline solutions of potassium permanganate and pyrogallol and then over incandescent copper. Before entering the three-necked flask it passes through a 40% solution of caustic soda. From the two-necked flask the hydrogen exits through the condenser, the upper end of which is connected through a three-way stopcock to the system of absorbing vessels arranged in series: two flasks containing a N/10 alkali solution and a Tishchenko with an alkaline solution of pyrogallol.

Into the first, three-necked flask, there is poured 60 ml of water. In the second, two-necked, flask, there are placed 1.0130 g of carefully pulverized ortho (α-chloropropionyl)-phenyl--glyoxylic acid, 2 g of semicarbazide hydrochloride, and 2 g of potassium acetate. 50 ml of a N/10 solution of caustic soda is placed in each of the absorbing flasks. The movable tube is

raised out of the three-necked flask until it no longer touches the surface of the water poured into the flask, and the stopcock of the tube connecting this flask to the two-necked flask is turned. Thus the second half of the apparatus is disconnected. Then hydrogen is passed through the apparatus to drive out the air in the first half of the system. After 1 hour of this, the water in the three-necked flask is heated to boiling and boiled for 30 minutes. Then the water is cooled, and, after closing with a clamp the exit opening of the condenser that is connected to the three-necked flask, the stopcock in the tube connecting the latter to the two-necked flask is opened, and the air throughout the system is driven out by hydrogen for 1 hour. The expelled air is let out into the atmosphere through the three-way stopcock. Then the three-way stopcock is turned to connect the system to the absorbers that contain aqueous solutions of alkali, and the hydrogen forces the water over to the two-necked flask after the sliding tube is pushed down to the bottom of the three-necked flask. From this moment on the experiment is continued for 24 hours at room temperature. The mixture of reagents in the two-necked flask is quickly dissolved in the water, and after 4.5 hours a white deposit of the semicarbazone of 2-methyl-indandione-1,3 (IX) begins to settle out gradually from the colorless solution. A slow current of hydrogen is passed through the system throughout the 24 hours of the test. After the 24 hours are up, the alkali in the absorbing flasks is titrated back with N/10 acid solution, first against phenolphthalein, and then against methyl orange.

The carbon dioxide formed during the reaction period consumed 19.50 of N/10 alkali solution, whereas 39.19 ml should have been used up according to computation. Hence, the yield of carbon dioxide is 49.76%.

The deposit of semicarbazone formed during the reaction is filtered out, washed with water, and air-dried. Its weight is 0.47 g, representing 51.8% of the theoretical. M.p.: 216-217° (decomp.). After triple recrystallization from alcohol it fuses at 231° (decomp.). A sample, mixed with the semicarbazone of 2-methyl-indandione-1,3 prepared in Experiment 6, fuses at the same temperature.

6. Preparation of the semicarbazone of 2-methyl-indandione-1,3 (IX). 0.12 g of 2-methyl--indandione-1,3 (V) is dissolved in 5 ml of alcohol, and a solution of 0.15 g of semicarbazide hydrochloride and 0.15 g of crystalline potassium acetate in 5 ml of water is added to the first solution. The solution turns dark yellow, and a white deposit begins to settle out within a few minutes. The next day the deposit is filtered out, washed with water, and air-dried. Weight: 0.16 g. M.p.: 229° (decomp.). Recrystallization from alcohol yields white crystals, which decompose at 231°. The yield is quantitative.

## CONCLUSIONS

The conditions and mechanism of the formation of five-membered and six-membered carboxylic compounds of ortho (α-chloropropionyl)-phenyl-glyoxylic acid were investigated. These transformations indicate the degree of complexity and variety of the secondary reactions that are undergone by the primary compounds formed as a result of the hydrolytic and oxidative-hydrolytic cleavages of quinones and cyclic polyketones.

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** C.B.English translation, 175-180.
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**** C.B. English translation, 447-455

# THE MECHANISM OF THE NITRATION OF THE AROMATIC COMPOUNDS OF NITRIC ACID

## II. RELATIVE ELECTRON POTENTIALS IN AROMATIC COMPOUNDS. MECHANISM OF THE NITRATION OF THE NITROPHENOLS

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According to the theory developed by us earlier [1], the activation energy of the formation of the transitional group of the nitrosation and nitration of aromatic compounds:

$$Ar-H + NOX \longrightarrow Ar\overset{\overset{+\delta}{\overset{H}{\cdots}}}{\underset{\underset{-\delta}{NOX}}{\cdots}}, \qquad (1)$$

(where NOX is the nitrating agent) may be represented as a first approximation by the expression:

$$E = E_0 - (\pi_{ArH} - \pi_{NOX}) \cdot \delta + R_{ArH} + R_{NOX}. \qquad (2)$$

in which $\pi$ denotes the mean electron potential of the interacting particles, and R = the energy consumed in changing the configuration of the corresponding molecules in the process of group formation.

If the value of the quantity $R_{ArH}$ is taken to be alike for a certain number of aromatic compounds, it is easy to prove that the velocity of their interaction with a given nitrating agent, such as, $NO_2$ or $[NO_2]^+$, the other conditions remaining the same, will be an extremely simple function of the value of $\pi$, viz:

$$\log K_{ArH} - \log K_{C_6H_6} = C_{NOX}(\pi_{ArH} - \pi_{C_6H_6}) \qquad (3)$$

or

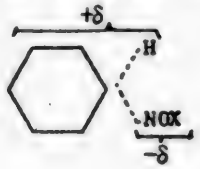
$$\log K_{ArH} = C_{NOX} \cdot \pi_{ArH} + C'_{NOX}. \qquad (4)$$

($C_{NOX}$ and $C'_{NOX}$ are constants.)

It should be noted that in these equations ArH signifies the condition of an aromatic compound in which it actually enters into a reaction; for example, for phenol it might be: $C_6H_5OH$ -- a neutral molecule; $C_6H_5O'$ — phenolate anion; $[C_6H_5OH_2]^+$ — phenyloxonium cation, etc.

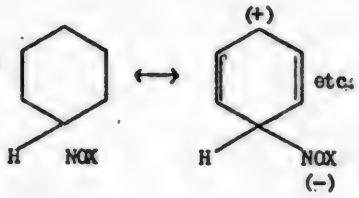
It follows from the foregoing that if our hypothesis were plausible, the value of the potentials $\pi_{ArH}$ would permit us to lay a theoretical foundation underneath experimental data and a different kind of observations on kinetic nitration and thus to make it possible to discover new phenomena in this field.

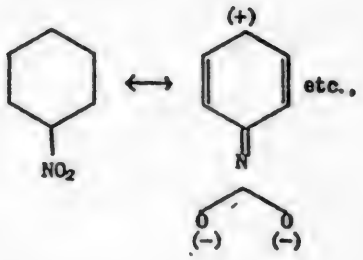
In our search for even approximate values of the potentials of aromatic compounds or of their differences, we employed the following line of reasoning, developed by us on general lines earlier [3]. It is evident from the diagrams of the electron structure of a transitional group (I) as well as of the end product of nitration (II):

(I) a) 

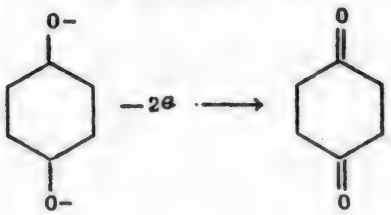

(II) a) $\overset{+\delta}{C_6H_5} \longrightarrow \overset{-\delta}{NO_2}$ (5)

or

(I) b) 


(II) b) 


that their formation is accompanied by the loss of electrons by the aromatic compound as a whole (I) or by its remnant (II), i.e., putting it differently, nitration is an oxidation reaction. Moreover, from the structural-chemical standpoint nitration corresponds to the oxidation of the benzenoid form to the quinonoid, as is shown by the resonance diagrams (I) b and (II) b; the mechanism of the oxidation of the hydroquinone anion:




(6)

in the ideal, simplified form reflects the nature of the electron transfer during nitration.

The similarity of the two reactions likewise applies to their kinetic characteristic. The influence of substituents upon the velocity of both reactions is quite identical, at least qualitatively, as will be proved below. If we start with our notions of the nature of the motive force of nitration, we find that the fundamental quantitative functions of both reactions will also be expressed in one form or another. At bottom, in accordance with the research of Dimroth [4], the constants (K) of the oxidation of para dihydroxy compounds to quinones are bound up with their normal potentials ($\pi$) by an equation of the same type as that discovered by us for nitration (cf. Equation 3), viz.:

$$\log K_n - \log K_0 = m(\pi_n - \pi_0), \quad (7)$$

in which the quantities $K_n$ and $\pi_n$ relate to any para dihydroxy compound, whereas $K_0$ and $\pi_0$ refer to the simplest hydroquinone, and m is a constant, whose value is 17.2.

This coincidence of the structural and kinetic characteristics of the two reactions permits us to assume that the oxidation potentials of paradihydroxy compounds vary parallel to the hypothetical potentials of the aromatic compounds that correspond to them; in the first approxim-

ation, it may be assumed that

$$\pi_n \approx q \cdot \pi_{ArH} .$$

where q = Coefficient of proportionality.

The values of $q \cdot \pi_{ArH} = \pi_n$ — we shall call them the relative chemical electron potentials in aromatic compounds — are listed for aromatic hydrocarbons and their mono derivatives in the following table [5], the potential of benzene itself, and hence the oxidation potential of para dihydroxybenzene being taken as equal to zero. For the analogs of benzene the positions to which these potentials correspond are shown; for the derivatives and homologs of benzene the ortho and para positions should be taken as such; for the meta positions, and, if the substituents are in another ring, the changes in potential constitute, according to a series of data, from 15 to 50% of those cited, but with the same sign; the quantities $q \cdot \pi_{ArH}$, found by extrapolation from related data, are listed in parentheses. The last column lists the relative electron potentials of aromatic compounds found from the critical oxidation potentials of substituted phenols. The coefficient of proportionality q′ of the second row is about twice as small as that of the first.

TABLE 1

Relative Electron Potentials in Aromatic Compounds

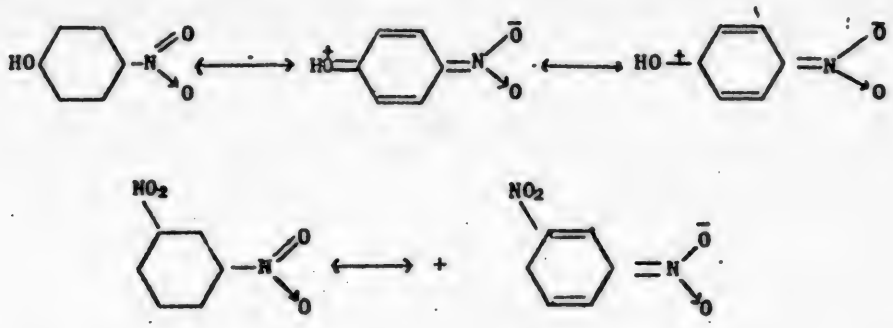
| Compound | $q \cdot \pi_{ArH}$ | $q' \cdot \pi_{ArH}$ | Compound | $q \cdot \pi_{ArH}$ | $q' \cdot \pi_{ArH}$ |
|---|---|---|---|---|---|
| Benzene | 0.00 | 0.00 | Aniline | 0.190 | |
| Alpha naphthalene | 0.231 | | Methyl aniline | 0.230 | |
| Beta naphthalene | 0.046 | | Acetanilide | 0.060 | |
| Meso anthracene | 0.561 | | Chlorobenzene | −0.016 | |
| Alpha anthracene | 0.314 | | Benzene sulfonic acid | −0.064 | |
| Beta anthracene | 0.176 | | Diphenyl sulfone | −0.120 | |
| 9,10-phenanthrene | 0.255 | | Acetophenone | (−0.120) | |
| Toluene | 0.052 | | Benzaldehyde | | −0.212 |
| Phenol | 0.112 | | Benzoic acid | (−0.100) | −0.268 |
| Anisole | 0.122 | 0.235 | Benzonitrile | (−0.140) | |
| Diphenyl ether | 0.019 | 0.059 | Nitrobenzene | (−0.160) | −0.344 |
| Phenyl acetate | 0.009 | | | | |

The differences in the heat of nitration agree with these data on the electron potential differences in aromatic compounds

$$\Delta Q = Q_{ArH} - Q_{C_6H_6}$$

| Compound | ΔQ in kilocal. |
|---|---|
| Naphthalene | 22.5 |
| Aniline | 18.0 |
| Phenol | 11.5 |
| Nitrobenzene | −3.3 |
| Meta dinitrobenzene | −7.8, etc. |

since the difference between the energy levels of the corresponding nitro compounds and that of nitrobenzene is due chiefly to their larger or smaller resonance of the following type:



We shall indicate the applicability of the quantities $\pi_{ArH}$ to chemical purposes by means of a number of examples. From a juxtaposition of experimental data the conclusion may be drawn that rapid nitration by nitrogen dioxide or by dilute nitric acid (via the intermediate reaction with nitrogen oxides) is feasible only with compounds having a relative potential of about +0.100 or higher. In agreement with this, naphthalene, anthracene, and phenanthrene react rapidly with the foregoing reagents, and moreover, in positions with maximum potential, whereas benzene and its mono alkyl substitutes practically do not react under these same conditions. From this standpoint we can also understand the ease with which the Ar — O — R alkyl-aryl ethers react with nitric acid in moderate concentrations in the presence of $NO_2$ and the difficulty of effecting analogous reactions with diphenyl ether, etc. etc. The causes for the decrease in the chemical activity of the ring upon the introduction of halogens, no matter whether they are ortho or para orienting substituents, likewise becomes clear.

Now let us consider the feasibility of nitration with nitric acid via the intermediate reaction of mono- and dinitro derivatives of aromatic compounds. It may be assumed as a first approximation that the decrease in potential associated with the introduction of the first nitro group will be identical in all cases, equaling the difference between the potentials of benzene and nitrobenzene, i.e., about 0.15. We accordingly found that nitronaphthalene and para nitrophenetole do not react with nitric acid, sp. gr. 1.2-1.4, containing nitrogen oxide. Contrary to this assertion to be proved, however, we found that ortho and para nitrophenols and even meta nitrophenol and 2,4-dinitrophenol are nitrated with relative ease by nitric acid under similar conditions, not reacting only if no nitrogen dioxide is present in the sphere of the reaction.

This contradiction between theory and practice was resolved with the aid of more detailed notions of the mechanism of nitration, which subsequently found convincing corroboration in practice. The essence of these concepts is as follows: Bearing in mind the acid nature of the nitrophenols and their tendency to dissociation:

$$NO_2C_6H_4OH \rightleftharpoons [NO_2C_6H_4O]' + H^{\cdot},$$

it was assumed that the initial reaction with the nitrogen dioxide involves not the nitrophenol itself, but the much more nucleophilic anion $[NO_2C_6H_4O]'$, which as such possesses a stepped-up [illegible]: $\pi_{[NO_2C_6H_4O]'} > \pi_{NO_2C_6H_4OH}$. The probability of the assumption concerning the entrance of the nitrophenols as anions into the reaction of nitration with nitrogen dioxide was demonstrated in two ways.

The first involved a comparison of the chemical activity of the nitrophenols and nitrophenolates with nitrogen dioxide dissolved in carbon tetrachloride or nitromethane. It was found that the nitrophenolates of the alkali metals, which doubtless possess the ionic structure $[NO_2C_6H_4O]'H^{\cdot}$, reacted very rapidly, with the evolution of heat, with nitrogen dioxide, being finally converted into the corresponding di- and trinitrophenols, whereas the free nitrophenols markedly did not react or entered into the reaction extremely slowly.

The second method of proof consisted of comparing the reaction velocity of ortho nitrophenol with nitrogen dioxide in solvents with greatly different ionizing ability. For this purpose we took, on the one hand, nitromethane with $\epsilon = 39.4$, in which the presence of the electrolytic dissociation of the nitrophenol was indicated by the appearance of a reddish color, due to the

formation of the nitrophenolate ion. The non-polar solvent employed was carbon tetrachloride, with $\epsilon = 2.2$, in which solutions of ortho nitrophenol were almost colorless. It was found that nitration to dinitrophenol took place very rapidly in a solution of nitromethane, in any event being completed within five minutes after the solutions were mixed together. In carbon tetrachloride, on the other hand, the reaction was only 50% complete even after standing for five hours. When 2,4-dinitrophenol was nitrated to picric acid in these same solvents, it was found that in the course of 12 days the reaction was nearly complete in nitromethane, whereas the yield of picric acid was less than 10% of the theoretical value in carbon tetrachloride (cf. the experimental section).

Our notions of the structural mechanism of nitration by nitric acid via reaction with the oxides of nitrogen were briefly outlined in our first paper. At low temperatures the reaction apparently takes place via the intermediate formation of nitroso derivatives. The activity of the nitrosating agents varies according to the following sequence:

$$[O{=}N]^+ > O{=}N{-}ONO_2 > O{=}N{-}ONO > O{=}N{-}OH.$$

In the simplest case, this mechanism may be represented by a diagram in which S denotes a molecule of the solvent or anion, e.g., $H_2O$, $CH_3NO_2$, $NO_3^-$:

$$Ar{-}H + [O{=}N]^+ \xrightarrow{S} \left[Ar\begin{matrix}H\cdots S\\ N{=}O\end{matrix}\right] \longrightarrow Ar{-}NO + [H\cdot S]^+$$

$$Ar{-}N{=}O + NO_2 \longrightarrow Ar{-}N\begin{matrix}=O\\ \cdots O{-}N{=}N\end{matrix} \longrightarrow Ar{-}NO_2 + NO.$$

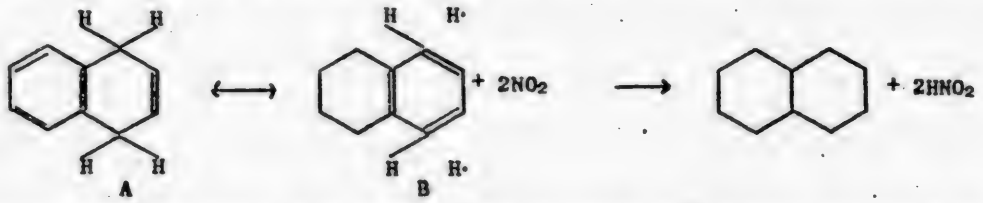
As the temperature is raised, the primary reaction with $NO_2$ begins to predominate, resulting in the formation of the singular organic analog of the monomer of nitrogen dioxide:

$$Ar{-}H + \cdot NO_2 \longrightarrow Ar\begin{matrix}H\cdot\\ NO_2\end{matrix} \longleftrightarrow \cdot Ar\begin{matrix}H\\ NO_2\end{matrix} \longleftrightarrow Ar\begin{matrix}H\\ \cdot NO_2\end{matrix}, \text{ etc.}$$

The transition from the latter to the nitro derivative is due to the participation of structure A with the atomized hydrogen atom in its resonance structure:

$$Ar\begin{matrix}H\cdot\\ NO_2\end{matrix} + \cdot NO_2 \longrightarrow Ar{-}NO_2 + HNO_2$$

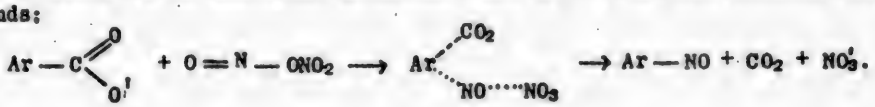
The plausibility of this sort of notion of the chemical nature of hydrogen in such crypto-aromatic compounds, as we call them, is confirmed by the ease with which hydrogen is split off from hydrogenated aromatic and heteroaromatic compounds when acted upon by oxides of nitrogen, as, for instance, dihydronaphthalene and the derivatives of dihydropyridine in the case of dihydrobenzene. The nature of reactions of this type may be represented by diagrams of the following type, in the symbols of resonance theory:



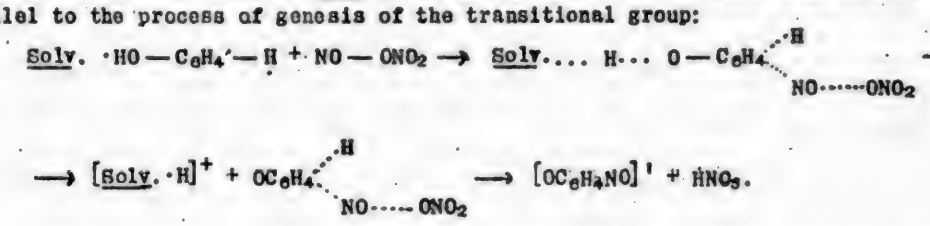

The participation of structure B in the resonance structure of a dihydro derivative reflects the tendency to form an aromatic system of bonds, resulting in weakening the bonds of the hydrogen atoms in the methylene group -- their atomization with the spin of their electrons maintained antiparallel. Dehydrogenation reactions of this sort with oxides of nitrogen are, of course, accompanied in some degree or other by side reactions.

There is no doubt that the deduction regarding the course of nitration reactions via the reaction of the corresponding anions with oxides of nitrogen may be applied to the appropriate case of the nitric-acid nitration of the phenols themselves and their substitutes, in particular, the phenol sulfonic acids, the aryl sulfanilides $Ar-SO_2-NH-Ar'$, and similar compounds, that are able to split off a hydrogen ion under the reaction conditions. It is probable that it is also applicable to some instances of nitration of the sulfo acids and carboxylic acids. Finally, we note that, in agreement with our experiment with V.V.Smirnov, the nitration by nitric acid of phenyldinitromethane $C_6H_5CH(NO_2)_2$ to phenyltrinitromethane $C_6H_5C(NO_2)_3$ likewise proceeds via the intermediate reaction of the nitrogen dioxide with the anion of the nitro compound or the acid form of the latter. These, as well as some other observations, justify the assumption that the usual method for the preparation of pseudonitrols and nitrolic acids is likewise based upon the primary reaction of the anion of the nitro compound with oxides of nitrogen or with nitrous acid.

Substitution of the carboxyl [3] and sulfo groups in the nitration of amino and phenol acids probably proceeds via an analogous mechanism, such as via the intermediate formation of nitroso compounds:



In nitration under conditions that do not favor ionization, as, for instance, in the medium of an organic solvent (Solv.), it may be supposed that the formation of anions proceeds parallel to the process of genesis of the transitional group:



The notions set forth in the present paper shed light upon some peculiarities of a number of the methods employed for nitration. Finally, it should likewise be noted that the results of our work can doubtless be applied to an understanding of many problems of other reactions: sulfonation, azo coupling, the Kolbe synthesis, condensation of phenols in an alkaline medium, etc. In all such cases, the formation of anions of aromatic compounds will raise their electron potential and, hence, the velocity of their reaction with electrophilic agents. The formation of the above-mentioned complexes and, even more so, of cations, taking place under the action of strong acids, will produce a contrary effect. An effect of this kind doubtless is often present in nitration: increasing the concentration of nitric acid or adding sulfuric acid or oleum may, on one hand, result in the appearance of a more energetic nitrating agent ($[NO_2]^+$), while, on the other hand, the formation of the above-mentioned complex from the aromatic compound may lower its ability to be nitrated. An instance of this sort of ambivalent influence of strong acids is dealt with in one of our papers [2].

## EXPERIMENTAL

(In association with A.N.Baryshnikova)

I. Proof of the absence of a reaction of para nitrophenetole and α-nitronaphthalene with concentrated nitric acid in the absence and in the presence of nitrogen oxides.

Two mixtures, each consisting of 1 g of the product and 5 ml of nitric acid, sp. gr. 1.37, with 0.05 g of hydrazine sulfate added to one of the mixtures to neutralize the traces of nitrogen oxides and 0.05 g of trioxymethylene to the other to ensure an appreciable content of nitrogen dioxide, were allowed to stand for 7 days under ordinary conditions. No signs of reaction were observed in either batch; the products subsequently isolated yielded no depression of the melting

point as such or in samples mixed with the initial products.

II. Proof of the course of nitration of nitro- and dinitrophenols by nitric acid via an intermediate reaction with nitrogen dioxide.

1. Experiments with nitrophenols. 1. g of para nitrophenol was mixed with 5 ml of nitric acid, sp. gr. 1.36, and 0.05 g of trioxymethylene, added to increase the percentage of nitrogen oxides.

No noticeable reaction was observed during mixing. Gradually, during the course of several hours, the para nitrophenol dissolved as a deposit of a different character settled out. Next day the reaction mass was diluted with water, and the product drawn off and washed with water. We obtained 0.73 g of 2,4-dinitrophenol with a m.p. of 102-107°, which when mixed with a test sample of the product known to be pure fused at 107-109°. In a parallel test, made without the addition of trioxymethylene, but with 0.3 g of hydrazine sulfate added, no marked changes occurred upon standing, and 0.56 g of pure para nitrophenol was recovered.

In the tests with meta nitrophenol, the reaction masses each consisted of 0.3 g of nitrophenol and 2 ml of nitric acid, sp. gr. 1.37, with 0.1 g of hydrazine sulfate added to one of them, and 0.01 g of trioxymethylene added to the other. In the first test, with no nitrogen oxides present, no noticeable changes occurred after five days of standing, and 0.2 g of pure meta nitrophenol was recovered. In the second test, with nitrogen dioxide present, the evolution of heat set in rapidly, all the meta nitrophenol was dissolved within a few minutes, and the dinitroproduct then separated out. 0.13 g of dinitrophenols with a m.p. of 88-89° was isolated; when mixed with a test sample of meta nitrophenol, a sharp depression of the melting point was observed.

Analogous results were obtained for the effect of nitrogen dioxide upon ortho nitrophenol.

2. Experiments with 2,4-dinitrophenol. Three mixtures of 1 g of 2,4-dinitrophenol and 40 ml of nitric acid, sp. gr 1.2, with 0.05 g of trioxymethylene added to the first, 0.5 g of urea nitrate added to the second, and 2 g of ammonium nitrate added to the third, were heated for 4 hours on a boiling water bath in flasks with ground in condensers. In each of the tests the deposit dissolved completely upon heating and settled out upon cooling.

In the first test, with nitrogen dioxide present in the reaction zone, 0.88 g of picric acid with a m.p. of 120-121° was isolated; it produced no depression in a mixed sample with the pure product.

In the second test, with nitrogen dioxide absent, 0.92 g of the pure, unchanged product was isolated, with a m.p. of 111-112°; it produced no depression of the melting point in a mixed test sample with 2,4-dinitrophenol and fused at about 85° when mixed with picric acid.

In the third test, slight nitration took place, owing to the incomplete elimination of the nitrogen oxides. 1.05 g of the product was obtained, with a m.p. of 105-108°; in a mixed sample with pure 2,4 dinitrophenol it fused at 107-109°.

III. Proof of the entrance of the nitrophenols into the nitration reaction as anions.

1. Investigation of the action of nitrogen dioxide upon the nitrophenols and nitrophenolates. a) 0.5 g of anhydrous sodium ortho nitrophenolate was mixed with 20 ml of anhydrous carbon tetrachloride, after which 10 ml of the solvent was driven off to eliminate any traces of moisture from the mixture. 1 ml of liquid nitrogen dioxide was added to the residue in the flask while it was stirred by hand. The temperature quickly rose to 12°. After 10 minutes of stirring 20 ml of water was added, and the whole subjected to steam distillation. No ortho nitrophenol was found in the distillate, while 0.43 g of a mixture of dinitrophenols with a m.p. of 96-100° was isolated from the residue in the flask. The bulk of the reaction product was 2,4-dinitrophenol, since it fused at 98-105° when mixed with a test sample that was known to be pure.

When a parallel test was run with ortho nitrophenol itself, no outward signs of a nitration reaction were observed. When the reaction mass was treated with reagents, 0.46 g of the initial

ortho nitrophenol was isolated 10 minutes after the reagents had been added. Only after standing for an hour did the reaction proceed to about 10% completion; we isolated 0.42 g of ortho nitrophenol and 0.05 g of dinitrophenol.

b) 1 ml of nitrogen dioxide was added under the above-described conditions to a mixture of 0.5 g of 2,4-dinitrophenolate of sodium and 10 ml of anhydrous nitromethane. The temperature rose gradually to 4°, and the nature of the deposit changed. After standing for an hour, the reaction mass was diluted with water and steam-distilled; 0.31 g of picric acid with a m.p. of 117-120° was isolated from the residue in the flask. It yielded no depression of the melting point when mixed with a test sample of the product that was known to be pure.

The formation of picric acid was not observed in a parallel test using free 2,4-dinitrophenol.

2. Investigation of the influence of the nature of the solvent upon the velocity of the reaction between nitrogen dioxide and the nitrophenols. a) Velocity with ortho nitrophenol. 1 g. of ortho nitrophenol was dissolved in 20 ml of the solvent, and then 1 ml of liquid nitrogen dioxide was added. After the reaction mass had been allowed to stand for a certain length of time 10 ml of water were added and the whole steam-distilled. Ortho nitrophenol was found in the distillate, and dinitrophenols in the residue.

When nitromethane is used as the solvent, the solution of ortho nitrophenol had a rather intense reddish color. The addition of nitrogen dioxide instantly caused the onset of the reaction, raising the temperature to 5°. Distillation after standing for 5 minutes indicated the complete absence of ortho nitrophenol. In the distilling flask there was left a dinitro product with a m.p. of 97-103°, which produced no depression when a mixed sample with 2,4-dinitrophenol was fused.

A solution of ortho nitrophenol in carbon tetrachloride was nearly colorless. Pouring in the nitrogen dioxide caused no noticeable rise in temperature. In Table 2 we give a summary of the test data with the varying duration of the reaction.

The products were identified by the melting points of test samples mixed with the pure products.

b) Tests with 2,4-dinitrophenol. 0.5 g of 2,4-dinitrophenol was dissolved in 10 ml of nitromethane in a small flask with a ground-glass stopper. The addition of 1 ml of nitrogen dioxide caused no noticeable increase in temperature, but in the course of 12 days the reaction was complete. After the solvent in the flask had been steam-distilled, 0.56 g of picric acid with a m.p of 118-120° was left behind in the flask; it was identified by the melting point of a test sample mixed with a product that was known to be pure.

In a parallel test using carbon tetrachloride instead of nitromethane we isolated 0.45 g of 2,4-dinitrophenol with a m.p. of 103-108°.

TABLE 2

| Time of standing | Ortho nitrophenol isolated | 2,4-dinitrophenol produced. |
|---|---|---|
| 5 minutes | 0.92 g, m.p. 46-48 | — |
| 1 hour | 0.82 g, m.p. 42-45 | 0.09 g, m.p. 92-97 |
| 3 hours | 0.64 g, m.p. 42-45 | 0.25 g, m.p. 93-98 |
| 5 hours | 0.50 g, m.p. 36-38 | 0.54 g, m.p. 95-100 |
| 2 days | — | 1.05 g, m.p. 93-98 |

In view of the incomplete dissolution of the dinitrophenol in 10 ml of carbon tetrachloride, a supplementary test was made, using 0.5 g of dinitrophenol in 70 ml of the solvent and 7 ml of nitrogen dioxide. After standing for 12 days, the reaction mass was subjected to prolonged steam distillation. After the solvent had been driven off, we collected 600 ml of aqueous distillate, which was then acidulated with 20 ml of concentrated hydrochloric acid, dried with

calcium chloride, and then extracted with ether. From the ether extract we isolated 0.26 g of 2,4-dinitrophenol with a m.p. of 106-109°, which was identified by means of a mixed test sample. The residue in the flask (about 7 ml) yielded only 0.03 g of picric acid with a m.p. of 118-120°. Thus, even in this case nitration in carbon tetrachloride was negligible.

## CONCLUSIONS

1. The nitration of aromatic compounds corresponds to the oxidation reaction of hydroquinones and quinones both in its electron-structural and its kinetic aspects.

2. Corresponding to Conclusion (1), the oxidation potentials of the hydroquinones may be employed as the relative electron potentials in aromatic compounds as introduced in the theory of nitration.

3. A link has been found between the velocity of nitration of aromatic compounds and their relative electron potentials.

4. It has been shown that nitration by nitric acid via an intermediate reaction with nitrogen dioxide is feasible only for the aromatic compounds that have a sufficiently high relative electron potential – of the order of 0.1 v.

5. Contrary to Conclusion (4), it has been found experimentally that the nitrophenols and dinitrophenols are nitrated by nitric acid via the intermediate reaction with nitrogen dioxide.

6. The observed contradiction between theory and experiment was resolved by assuming that the nitrophenols enter into the reaction as nitrophenolate ions; this was corroborated by the experimental investigation of the velocity of the nitration of the nitrophenols and nitrophenolates by nitrogen dioxide and the effect of the ionizing power of the solvent upon the reaction velocity.

7. In the development of Conclusion (5) new concepts of the mechanism of nitration of the phenols and their derivatives in the ring, of aryl sulfanilides, carboxylic acids, and sulfo acids, as well as the substitution reaction of the nitro group for carboxyl in the aromatic hydroxy acids and for the sulfo group in aryl sulfonic acids, were set forth.

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# ABSORPTION AND REMOVAL OF WATER FROM CASEIN

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A sample of casein (10 g) was initially dried in a desiccator over $H_2SO_4$ at room temperature and atmospheric pressure. Periodically (intervals of several days), the sample was weighed until the loss in weight ceased. This took place after 85 days (August 16 – November 10, 1944). The weighing bottle of casein was then dried in a vacuum. The change in weight ceased after 147 days (January 11, 1945). The weighing bottle was then placed in a thermostat at 65–70° for 6 hours in one day, for 10 days – at 80–90° and then for 13 days – at 100–110°. The experiment was completed in 11 days (February 15, 1945), since the weight no longer changed. The total duration of the experiment was 181 days. The weight of casein at this time was 8.5383 g, a loss of 1.4617 g (14.62%).

The reverse experiment, that of absorption of moisture, was then carried out with the same sample, in which the weighing bottle was placed in a desiccator without $H_2SO_4$ at room temperature and atmospheric pressure. The experiment lasted 178 days (to August 1[illegible], 1945), when the weight ceased to increase. The weight of casein at this time was 9.3967 g; the increase – 0.8584 g (8.58%). The weighings were made every 3–4 days; at an increased temperature, every 1–2 days (sometimes every 8 days). The results were further combined into a longer period of time (the number of days were chosen approximately equal to the squares of whole numbers: 4, 9, 16, 25 etc.). As shown by preliminary experiments, to derive equations of the curves for absorption and release of water, $\sqrt{x}$ had to be used, where x is the time. Actually, it was often necessary to use $\sqrt[4]{x}$.

The results of the weighings are given in Tables 1, 2 and 3.

The experiment with the release of water was repeated analogous to the first experiment (Table 1), but with another preparation of casein; the data are given in Table 3.

The absolute values for the decrease in weight in this experiment differ from the first experiment (Table 1), but the relative change in this decrease is the same.

The results of Table 1 give a curve, corresponding to the equation $y = 1 + \frac{\sqrt[4]{x}}{10}$, the results of Table 2 correspond to the equation $y = \frac{\sqrt{x}}{10}$ (for the first month of the experiment) and $y = \frac{\sqrt[4]{x}}{5}$ (for the remaining time), the results of Table 3 – the equation $y = \frac{\sqrt{x}}{5}$; the general formula being $y = \frac{\sqrt[n]{x}}{m}$ and $y = 1 + \frac{\sqrt[n]{x}}{m}$, where $n = 2$ and 4, and $m = 5$ and 10.

If the quantity of released and absorbed water is expressed in moles, we then obtain the following number of moles (based on $10^5$ grams of protein).

According to Pauling et al., the number of moles of water is almost equal to the number of polar groups of several amino acids in the protein (serine, threonine, oxyproline, tyrosine, histidine, tryptophane, lysine, arginine, asparagine, glutamic and oxyglutamic acids); therefore, the number of polar groups may be judged by the number of moles of water.

The presence of approximately 350–475 polar groups may be concluded from the 2nd and 3rd experiments (Tables 2 and 3). In the 1st experiment (Table 1), a greater number was obtained

TABLE 1

Release of Water from Casein

| Days (x) | Weight (g) | Loss in weight (g) (y) | $\sqrt{x}$ | $\sqrt[4]{x}$ | $y = 1 + \frac{\sqrt[4]{x}}{10}$ |
|---|---|---|---|---|---|
| 0 | 10 | 0 | 0 | 0 | — |
| 3 | 9.0493 | 0.950 | 1.7 | 1.3 | 1.13 |
| 10 | 8.8111 | 1.1889 | 3.0 | 1.7 | 1.17 |
| 17 | 8.7673 | 1.2327 | 4.0 | 2.0 | 1.20 |
| 24 | 8.7471 | 1.2529 | 5.0 | 2.25 | 1.225 |
| 35 | 8.7334 | 1.2666 | 6.0 | 2.5 | 1.25 |
| 49 | 8.7276 | 1.2724 | 7.0 | 2.7 | 1.27 |
| 53 | 8.7253 | 1.2747 | 8.0 | 2.8 | 1.28 |
| 85 | 8.7245 | 1.2755 | 9.3 | 3.0 | 1.30 |
| | | Vacuum | | | |
| 89 | 8.7223 | 1.2777 | — | — | — |
| 97 | 8.7179 | 1.2821 | — | — | — |
| 101 | 8.7156 | 1.2844 | — | — | — |
| 108 | 8.7119 | 1.2881 | — | — | — |
| 122 | 8.7067 | 1.2933 | — | — | — |
| 133 | 8.7061 | 1.2939 | — | — | — |
| 147 | 8.7059 | 1.2941 | — | — | — |
| | 65–70° | | — | — | — |
| 157 | 8.6454 | 1.3546 | — | — | — |
| | 80–90° | | | | |
| 170 | 8.5481 | 1.4519 | — | — | — |
| | 100–110° | | — | — | — |
| 181 | 8.5383 | 1.4617 | — | — | — |

TABLE 2

Absorption of Water by Casein

| Days (x) | Weight (g) | Increase in weight (g) (y) | $\sqrt{x}$ | $\sqrt[4]{x}$ | $y = \frac{\sqrt{x}}{10}$ | $y = \frac{\sqrt[4]{x}}{5}$ |
|---|---|---|---|---|---|---|
| 0 | 8.5383 | 0 | 0 | 0 | 0 | 0 |
| 2 | 8.6833 | 0.1450 | 1.4 | 1.2 | 0.14 | 0.24 |
| 6 | 8.7265 | 0.1832 | 2.1 | 1.5 | 0.25 | 0.30 |
| 9 | 8.7740 | 0.2357 | 3.0 | 1.7 | 0.30 | 0.34 |
| 16 | 8.9337 | 0.3954 | 4.0 | 2.0 | 0.40 | 0.40 |
| 27 | 8.9805 | 0.4422 | 5.2 | 2.3 | 0.50 | 0.46 |
| 37 | 9.0189 | 0.4806 | 6.0 | 2.5 | 0.60 | 0.50 |
| 48 | 9.0327 | 0.4944 | 7.0 | 2.7 | 0.70 | 0.54 |
| 65 | 9.0773 | 0.5390 | 8.0 | 2.8 | 0.80 | 0.56 |
| 79 | 9.1057 | 0.5674 | 9.0 | 3.0 | 0.90 | 0.60 |
| 101 | 9.1741 | 0.6358 | 10.1 | 3.15 | 1.0 | 0.63 |
| 122 | 9.1961 | 0.6578 | 11.0 | 3.3 | 1.1 | 0.66 |
| 147 | 9.2907 | 0.7524 | 12.0 | 3.5 | 1.2 | 0.70 |
| 178 | 9.3967 | 0.8584 | 13.5 | 3.65 | 1.35 | 0.73 |

than in the 2nd and 3rd (1709 moles of water in 85 days; later we will omit this number for comparison with another experiment, in which the drying in vacuum and in a thermostat did not take place). The first preparation (experiment 1) was more moist than the second preparation (experiment 3). It can be supposed that other factors entered into the fixation of the water (perhaps, according to Sponsler et al.[2], carbonyl peptide compounds, hydrogen compounds). Besides, the change in weight upon drying in the thermostat could have partially occurred, not only by the release of moisture, but also as a result of a partial decomposition of the substance; therefore we did not calculate the water on a molar basis after 147 days of the first experiment.

TABLE 3

| Days (x) | Weight (g) | Loss in weight (g) (y) | $\sqrt{x}$ | $\sqrt[4]{x}$ | $y = \frac{\sqrt[4]{x}}{5}$ |
|---|---|---|---|---|---|
| 0 | 10.0 | 0 | 0 | 0 | 0 |
| 3 | 9.6244 | 0.3756 | 1.7 | 1.3 | 0.26 |
| 10 | 9.5234 | 0.4766 | 3.0 | 1.7 | 0.34 |
| 15 | 9.4822 | 0.5178 | 4.0 | 2.0 | 0.40 |
| 24 | 9.4510 | 0.5490 | 5.0 | 2.25 | 0.45 |
| 35 | 9.4420 | 0.5580 | 6.0 | 2.5 | 0.50 |
| 49 | 9.4310 | 0.5690 | 7.0 | 2.7 | 0.54 |
| 63 | 9.4210 | 0.5790 | 8.0 | 2.8 | 0.56 |
| 84 | 9.4086 | 0.5914 | 9.2 | 3.0 | 0.60 |
| 103 | 9.3868 | 0.6132 | 10.2 | 3.2 | 0.64 |
| 122 | 9.3790 | 0.6210 | 11.0 | 3.3 | 0.66 |
| 143 | 9.3690 | 0.6310 | 12.0 | 3.5 | 0.70 |
| 164 | 9.3686 | 0.6314 | 12.8 | 3.6 | 0.72 |

TABLE 4

| Days | According to Table 1 (release of water) | According to Table 2 (absorption of water) | According to Table 3 (release of water) |
|---|---|---|---|
| 2,3 | 528 | 80 | 209 |
| 6 | — | 104 | – |
| 9; 10 | 660 | 131 | 265 |
| 15, 16, 17 | 685 | 220 | 288 |
| 24, 27 | 696 | 246 | 305 |
| 35, 37 | 704 | 267 | 310 |
| 48, 49 | 707 | 275 | 316 |
| 63, 65 | 708 | 300 | 322 |
| 79, 84, 85 | 709 | 315 | 329 |
| 101, 108 | 714 | 353 | 341 |
| 122 | 718 | 365 | 345 |
| 143, 147 | 719 | 418 | 350 |
| 164 | — | — | 351 |
| 178 | — | 477 | — |

The number of polar groups participating in the absorption and release of water in a period of time are seen from the 2nd column of Table 4 (absorption of water) and from the 3rd column of the same table (release of water). With an increase in the time of absorption and release of water, the number of polar groups participating in the absorption increases, being smaller at first and only later (after 100 days) greater than the release of water (in

the 1st experiment – 1st column, Table 4 – all the figures are greater than in the second column). Thus, the release of the greater part of the water takes place more energetically than the absorption.

## Conclusions

1. In the first day, casein releases water comparatively quickly, then very slowly.

2. The reverse absorption of water takes place at first more quickly, then very slowly and does not reach the previous level.

3. The curves for the release and absorption of water may be expressed by the general equation $y = \gamma - \frac{\sqrt[n]{x}}{m}$ or $y = 1 + \frac{\sqrt[n]{x}}{m}$, where $n = 2$ or 4, $m = 5$ or 10. ($y = 1 + \frac{\sqrt{x}}{10}$, $y = \frac{\sqrt[4]{x}}{5}$, $Y = \frac{\sqrt{x}}{5}$)

4 The amount of absorbed and released water in our experiments is expressed by approximately 350 - 475 moles.

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# SULFONATION AND SULFONIC ACIDS OF ACIDOPHOBIC COMPOUNDS

## II. SULFONATION OF THE FURAN HOMOLOGS

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In a previous paper [1] it was shown that we could sulfonate furan with a quantitative yield, using pyridine-sulfotrioxide. Our next problem was the extension of this method to the sulfonation of the furan homologs, which, like their parent compound are extremely acidophobic (easily resinifies with acids), as a result of which their sulfo-derivatives are not known. The object of the present paper is the sulfonation of sylvan, dimethylfuran and coumarone.

Like furan, all its homologs react with pyridine-sulfotrioxide without resinification. Upon heating for 8-10 hours at a temperature of 100°, their sulfonic acids are formed, usually with very high yields. Thus, for the first time, sulfoderivatives of sylvan, 2,5-dimethyl-furan and coumarone were successfully obtained.

Sulfonation of sylvan. For the sulfonation we used both technical sylvan from wood tar and synthetic sylvan, obtained from furfural by the Kishner reaction [2]. The reaction of sylvan with pyridine-sulfotrioxide under the conditions for the sulfonation of furan led to the formation of disulfoderivatives, separated as the barium salt. The barium salt of the disulfonic acid thus obtained holds its water of crystallization very strongly and releases it only upon boiling with toluene. The structure of the disulfonic acid of sylvan is determined by oxidation with bromine water; barium sulfate precipitated in the cold, the quantity of which corresponded with the splitting off of one sulfogroup; the second sulfogroup was situated in the β-position and according to the orientation rule of the furan ring it is obvious that it is found in the ortho-position to the methyl group.

Monosulfosylvan can be obtained under milder conditions of sulfonation; upon carrying out the reaction at a temperature of 30-40° for two weeks in a dichlorethane medium or with excess sylvan. The sylvansulfonic acid formed was separated as the barium salt and determined by oxidation with bromine water; the first drops of bromine water even in the cold caused a precipitation of barium sulfate. From the filtrate acetylacrylic acid was separated, identified by its melting point. Like the barium salt of disulfosylvan, this salt also holds its water of crystallization very strongly, not releasing it upon boiling the substance with benzene. Boiling with toluene leads to a charring of the salt. Sylvansulfonic acid, like furan-sulfonic acid, does not change upon boiling with concentrated solutions of alkalies and hydrolyzes relatively easily upon boiling with acids, with the formation of sulfur dioxide.

2,5-Dimethylfuran was obtained from methylfurfural by the Kishner reaction [2]. Under the usual sulfonation conditions, it reacts with the formation of monosulfoderivatives, the sulfogroup of which is evidently situated in the β-position of the furan ring. A precipitate of barium sulfate does not form by the action of bromine water, even upon prolonged heating; and if there were any doubt that the β-sulfogroup is stable toward oxidizing agents, it would be dispelled by investigations of the properties of the sulfonic acid of dimethylfuran in which it was shown that a precipitate of barium sulfate was definite proof of an α-position of the sulfo-group. Upon boiling

with alkalies, the sulfoacid of dimethylfuran did not change. On the other hand, it hydrolyzed upon boiling with acids, like the other sulfoacids of the furan series, with the formation of sulfur dioxide, although the hydrolysis took place much slower.

Coumarone has a furan ring in its system and therefore is similar to furan in many reactions: it is also stable towards alkalies and, on the other hand, easily changes upon the action of mineral acids. It forms resins by the action of sulfuric acid, technically known by the term "coumarone resins". Concerning coumarone, not much is known of reactions involving the direct substitution of hydrogens in the furan ring. Like the true furans, these reactions take place principally in a non-aqueous medium: the nitration of coumarone is conducted in glacial acetic acid (with a very slight yield [3]); the action of concentrated sulfuric acid at -10° upon crude coal-tar benzene, containing some coumarone, leads to the formation of little-known derivatives from the sulfonation of coumarone, from which the pure coumarone is extracted by distillation with live steam.

In view of the extreme scarcity of substitution reactions with coumarone, it was considered of great interest to obtain sulfocoumarone by the action of pyridine-sulfotrioxide, the more so since sulfocoumarone has not been separated in the pure state nor has it been described.

Coumarone, upon heating with pyridine-sulfotrioxide at 100° for 10 hours gives a quantitative yield of sulfocoumarone, separated in the form of its barium salt. Analyses of the barium and sodium salts correspond to the monosulfoacid of coumarone. The sulfogroup is located in the α-position of the furan nucleus, since upon oxidation, the barium salt of coumaronesulfonic acid was converted into barium sulfate, and from the filtrate the lactone of o-oxyphenylacetic acid was separated. Like sulfocompounds of the furan series, coumarone-sulfonic acid is stable upon boiling with alkalies, but is distinguished from them by hydrolyzing with acids to form sulfuric acid and coumarone analogously to the sulfocompounds of the benzene series. Consequently, for coumarone as well as for furan and its homologs, the reaction with pyridine-sulfotrioxide took place without resinification and with a good yield, in contradistinction to other substitution reactions of the hydrogens of the furan ring.

Besides the compounds described, we sulfonated a series of compounds of the benzene series. It was shown that neither benzene nor its homologs could be sulfonated by pyridine-sulfotrioxide in any considerable quantity. Then, we sulfonated several compounds of the furan series: furfural, the methyl ether of furyl alcohol and pyromucic acid.

Furfural did not react with pyridine-sulfotrioxide, remaining unchanged upon heating for several hours at 120°, and charred upon heating to 150-160°.

Pyromucic acid reacted with pyridine-sulfotrioxide only at 140°, forming α-sulfofuran with a splitting of the carboxyl group.

Attempts to sulfonate the methyl ether of furyl alcohol were, unfortunately, unsuccessful: resinification took place both by the direct action of pyridine-sulfotrioxide and in a solution of dichloroethane. We do not lose hope that a more detailed study of this reaction will disclose conditions for the sulfonation of derivatives of furyl alcohol, which would hold out the possibility of greater yields.

## EXPERIMENTAL

Technical sylvan was obtained from a wood-pulp works (reddish-brown liquid), washed with bisulfite, alkali and water, dried over calcium chloride, then with metallic sodium and distilled over metallic sodium. B.p. 62-63°; $n_D^{20}$ 1.4321; $d_4^{20}$ 0.902.

Synthetic sylvan was obtained by the Kishner [2] reaction from furfural. From 20 g. of distilled furfural and 10.5 g of hydrazine hydrate, the hydrazone was obtained, which was then decomposed by alkali. 2 g of sodium hydroxide was placed in a Claisen flask which was furnished with a dropping funnel and connected with a condenser. The hydrazone was added from the dropping funnel at such a rate as not to make the reaction too violent. 8 g of sylvan were obtained, which was distilled over metallic mercury. B.p. 63 - 65°, $n_D^{20}$ 1.4338; $d_4^{20}$ 0.9152.

The sulfonation of sylvan at a temperature of 100° always leads to the formation of sylvan disulfonic acid, being independent of the amount of pyridine-sulfotrioxide taken. The purified technical sylvan was heated with pyridine-sulfotrioxide in a sealed ampoule at a temperature of 100° for 10 hours. The sulfomixture, a dark-brown, was treated with a suspension of barium carbonate with warming on a water bath for 40-60 minutes. The barium sulfate and excess barium carbonate were filtered off on a Buchner funnel and washed with hot water. The dark-brown filtrate was decolorized by boiling with activated carbon, evaporated and the barium salt precipitated from a concentrated solution of alcohol. The experimental data are shown in the table.

| Sylvan (g) | Pyridine-sulfotrioxide (g) | Ratio | Ba-salt obtained (g) | Yield (in %) |
|---|---|---|---|---|
| 1.8 | 3.3 | 1:1 | 1.8 | 20 |
| 2.5 | 10. | 1:2 | 4.7 | 37 |
| 4.5 | 26.4 | 1:3 | 17.8 | 77.5 |

Upon sulfonation of technical sylvan, there always remained some liquid which did not enter into the reaction (obviously, not reacting with the pyridine-sulfotrioxide mixture).

The barium salt of sylvansulfonic acid forms white crystals, very soluble in water, soluble with difficulty in alcohol and insoluble in other organic solvents.

11.156 mg substance: 6.274 mg $BaSO_4$.
7.154 mg substance: 4.012 mg $BaSO_4$.
Found %: Ba 33.11, 33.09.
$C_5H_4O_7S_2Ba \cdot 2H_2O$. Calculated %: Ba 33.22.

The dehydration of the barium salt by simple heating could not be accomplished, since charring took place upon heating over 100°. The removal of water of crystallization was realized by boiling with toluene and evaporating of the latter until the complete removal of water was accomplished. The salt thus formed was washed with ether, dried and analyzed:

11.020 mg substance: 6.813 mg $BaSO_4$.
7.588 mg substance: 4.689 mg $BaSO_4$.
Found %: Ba 36.38, 36.37.
$C_5H_4O_7S_2Ba$. Calculated %: Ba 36.39.

6.350 mg substance: 3.724 mg $CO_2$: 0.700 mg $H_2O$.
4.190 mg substance: 2.460 mg $CO_2$: 0.500 mg $H_2O$.
Found %: C 15.99, 16.05; H 1.23, 1.34.
$C_5H_4O_7S_2Ba$. Calculated %: C 15.91; H 1.07.

Sulfonation of synthetic sylvan gave much higher yields of the disulfonic acid and did not require decolorization of the filtrate after treating with barium carbonate. Sulfonation of unpurified technical sylvan led to a large degree of resinification and a poor yield of the barium salt.

The sodium salt of sylvandisulfonic acid was obtained by precipitating the barium from solutions of the barium salt by sodium carbonate. The sodium salt - crystals of a white color, easily soluble in water, somewhat in alcohol and insoluble in other organic solvents. For analysis of the salt, it was twice precipitated from water with alcohol.

4.711 mg substance: 2.319 mg $Na_2SO_4$.
5.825 mg substance: 2.825 mg $Na_2SO_4$.
Found %: Na 15.95, 15.71.
$C_5H_4O_7S_2Na_2$. Calculated %: Na 16.02.

The silver and potassium salts of sylvandisulfonic acid were obtained. The first - soluble with difficulty, the precipitate darkening quickly in air. The salts of these organic bases are easily soluble in alcohol as well as in water.

Sylvandisulfonic acid. Barium is precipitated from a solution of the barium salt by a calculated quantity of sulfuric acid. Evaporating the filtrate on a water bath led to charring

as in the case with furansulfonic acid. Careful evaporation in a vacuum desiccator produced a dark, very hygroscopic liquid.

Structure of the disulfonic acid of sylvan. Bromine water in the cold yielded a precipitate of barium sulfate from a solution of the barium salt of sylvandisulfonic acid.

2.0 grams of the barium salt of sylvandisulfonic acid was oxidized with bromine water in the cold until the precipitation of barium sulfate was complete and the bromine color remained permanent. The barium salt was filtered off, washed, dried, ignited and weighed. The weight of barium sulfate was 0.850 g. The yield, figuring on one sulfogroup, as 76%. The remaining oxidation products were not separated.

Monosulfosylvan was obtained by a mild sulfonation of sylvan in a dichlorethane medium or sylvan itself. 2.0 g of sylvan, 3.9 g of pyridine-sulfotrioxide and 15 ml of dichlorethane, sealed in an ampoule, was allowed to remain at room temperature for a month. The sulfomixture was treated as usual. 3.5 g of the barium salt of monosulfosylvan was obtained. The yield, figuring on five waters of crystallization, was about 50%. The barium salt – light yellow crystals, easily soluble in alcohol as well as in water. For the analysis, the salt was twice recrystallized from water. A partial dehydration took place upon boiling in benzene.

7.395 mg substance: 3.440 mg $BaSO_4$
6.755 mg substance: 3.170 mg $BaSO_4$
Found %: Ba 27.39, 27.62.
$C_{10}H_{10}O_8S_2Ba \cdot 2H_2O$. Calculated %: Ba 27.67.

A complete dehydration of the salt could not be accomplished, since boiling in toluene led to a charring of the material.

Structure of the monosulfonic acid of sylvan. The first drops of bromine caused a precipitation of barium sulfate from a solution of the barium salt. 2.0 g of the barium salt of monosulfosylvan was dissolved in 15 ml of water and bromine water added until the precipitation of barium sulfate was completed. The latter was filtered, dried and ignited. The weight of barium sulfate was 0.847 g. The yield, on a basis of barium, was 84%. From the filtrate, shiny white crystals of acetylacrylic acid was extracted with ether. M.p. 122°; from the data in the literature: m.p. 125° [5].

Hydrolysis with acids. Upon boiling the barium salts, – disulfosylvan as well as monosulfosylvan – with 25% hydrochloric acid in a flask with a reflux condenser for four hours, sulfurous acid was separated which was detected by its odor and by oxidation with bromine water to sulfuric acid and identification of the latter as barium sulfate.

2,5-Dimethylfuran was obtained by the Kishner reaction [2] from methyl furfural. Upon cooling, the hydrazone was obtained from 10 grams of methylfurfural and 4.5 g of hydrazine hydrate. Decomposition of the hydrazone was carried out in a Claisen flask furnished with a dropping funnel and a straight condenser. 2.0 g of potassium hydroxide was placed in the flask; the hydrazone was added at such a rate as not to cause a too violent reaction. 7.0 g of 2,5-dimethylfuran was obtained. The yield, on the basis of methylfurfural, was 80.5%. B.p. 94–96°; $n_D^{20}$ 1.4450; $d_4^{20}$ 0.9033.

Sulfonation of 2,5-dimethylfuran was carried out by heating in a sealed ampoule at a temperature of 100° for 10 hours. Treatment of the sulfomixture was as usual. The barium salt – white crystals, easily soluble in water, with difficulty in alcohol and organic solvents. For analysis, the salt was twice recrystallized from water.

7.182 mg substance: 3.412 mg $BaSO_4$
5.180 mg substance: 2.590 mg $BaSO_4$
Found %: Ba 27.97, 28.32.
$C_{12}H_{14}O_8S_2Ba$. Calculated %: Ba 28.16.

4.330 mg substance: 4.713 mg $CO_2$; 1.122 mg $H_2O$.
5.890 mg substance: 6.388 mg $CO_2$; 1.510 mg $H_2O$.
Found %: C 29.69, 29.58; H 2.90, 2.86.
$C_{12}H_{14}O_8S_2Ba$. Calculated %: C 29.56; H 2.89.

The sodium salt of the sulfonicacid of dimethylfuran was obtained from the barium salt by

the action of soda. For analysis, the salt was twice recrystallized from water with alcohol.

6.397 mg substance: 2.335 mg $Na_2SO_4$
Found %: Na 11.82.
$C_6H_7O_4SNa$. Calculated %: Na 11.60.

Structure of the sulfonic acid of 2,5-dimethylfuran. Upon adding bromine water to a solution of the barium salt of the sulfonic acid of dimethylfuran, decolorization took place, but a splitting off of the sulfogroup was not observed even after prolonged heating.

Hydrolysis with acids. Upon boiling the barium salt of the sulfonic acid of dimethylfuran with 25% hydrochloric acid for 8 hours, sulfur dioxide gas was evolved, which was detected by its odor and then identified by conversion to sulfuric acid.

Sulfonation of Coumarone. 2.2 g of coumarone and 7.5 g of pyridine-sulfotrioxide were heated at 100° for 10 hours. The treatment of the sulfomixture was a usual. 5.0 g of the barium salt was obtained. The yield was quantitative. The barium salt – shiny, white crystals, somewhat less soluble in water than the barium salt of furan sulfonic acids. For analysis, the barium salt was twice recrystallized from water.

4.095 mg substance: 1.763 mg $BaSO_4$
4.573 mg substance: 1.965 mg $BaSO_4$
Found %: Ba 25.34, 25.38.
$C_{16}H_{10}O_8S_2Ba$. Calculated %: Ba 25.84.

5.510 mg substance: 7.340 mg $CO_2$; 1.135 mg $H_2O$.
6.090 mg substance: 8.100 mg $CO_2$; 1.150 mg $H_2O$.
Found %: C 36.33, 36.23; H 2.30, 2.11.
$C_{16}H_{10}O_8S_2Ba$. Calculated %: C 36.13; H 1.90.

The sodium salt of coumarone sulfonic acid was obtained in the usual fashion. White crystals, easily soluble in water.

4.698 mg substance: 1.544 mg $Na_2SO_4$
Found %: Na 10.64
$C_8H_5O_4SNa$. Calculated %: Na 10.45.

Structure of coumarone sulfonic acid. 1.0 g of the barium salt was dissolved in 15 ml of distilled water. Bromine water was added until the color did not disappear. At first an insignificant amount of barium sulfate precipitated, which increased markedly upon heating. From the filtrate, the lactone of o-oxyphenylacetic acid was extracted by ether, as partially congealed crystals with a m.p. of 47°; data from the literature: m.p. 49° [6].

Hydrolysis with acids. Upon boiling the barium salt of coumarone-sulfonic acid with 25% hydrochloric acid in a flask with a reflux condenser for 4 hours, a separation of barium sulfate and coumarone occurred.

Furfural. Even upon prolonged heating in a sealed ampoule, pyridine-sulfotrioxide did not react with furfural; the major portion of the latter remained unchanged.

5 g of furfural and 8.3 g of pyridine-sulfotrioxide was heated for 20 hours at 100°. The furfural not taking part in the reaction (4.3 g) was distilled, and the remainder treated with a paste of barium carbonate. The filtrate did not give a reaction for barium.

Methyl ether of furyl alcohol resinified upon heating with pyridine-sulfotrioxide. The filtrate after treatment with barium carbonate gave only a weak reaction for barium. The barium salt which separated after evaporation darkened quickly in air. Sulfonation in a dichlorethane medium led to the same results.

Pyromucic acid reacted with pyridine-sulfotrioxide under the usual conditions for the sulfonation of furan compounds (heating for 8 hours at a temperature of 100°), but not giving sulfoderivatives. Heating for 10 hours at a temperature of 140° led to a cleavage of the carboxyl group and the formation of furansulfonic acid.

1.0 g of pyromucic acid, 4.2 g of pyridine-sulfotrioxide and 20 ml of chlorbenzene were heated for 10 hours under a reflux condenser. A gas was evolved which was identified by the clouding of baryta water ($CO_2$). The sulfomixture was treated with a paste of barium carbonate. The filtrate was evaporated to a small volume and the barium salt precipitated with alcohol. It

gave a precipitate of barium sulfate with bromine water in the cold, which served to indicate the α-position of the sulfogroup. With S-benzilthiuranchloride, shiny white crystals with a m.p. of 205° were formed, which were difficultly soluble in water. The obtained barium salt of furansulfonic acid was 1.2 g, with is 63%, calculated from pyromucic acid.

## CONCLUSIONS

1. By the action of pyridine-sulfotrioxide on 2-methylfuran, 2,5-dimethylfuran and coumarone, the sulfonic acids of these compounds were obtained, separated as the barium and sodium salts. Thus, there were obtained for the first time 2-methylfuransulfonic acid-(5), 2-methylfurandisulfonic acid-(3,5), 2,5-dimethylfuransulfonic acid-(3) and coumaronesulfonic acid-(2), the structures of which were shown by the cleavage with bromine water.

2. Attempts to sulfonate functional derivatives of furan containing oxygen, showed that the methyl ether of furyl alcohol resinifies when treated with pyridine-sulfotrioxide, furfural does not react under the usual conditions, and with pyromucic acid a substitution of the carboxyl group by sulfonic acid took place.

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# SULFONATION AND SULFONIC ACIDS OF ACIDOPHOBIC COMPOUNDS

## III. SULFONATION OF PYRROLE AND ITS HOMOLOGS

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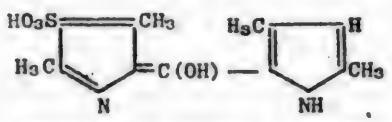
In a previous paper by A. Terent'ev and L. Kazitsina [1] it was shown that with the aid of the reaction product of sulfuric anhydride with pyridine (pyridine-sulfotrioxide), it was possible to sulfonate those substances which would completely resinify with the other, usual sulfonation agents. Excellent yields of sulfonic acids were obtained for a series of furan derivatives.

The present paper concerns the sulfonation of pyrrole and its homologs, and also two of its aryl substitution products. The initial experiments on the sulfonation of pyrrole were described in a previous paper by Terent'ev and Shadkin [2].

Several examples of the sulfonation of pyrrole derivatives are quite well known. In 1885 Ciamician and Silber sulfonated α-acetylpyrrole by treating it with sulfuric acid vapor [3]. By this method they separated and analyzed the potassium salt of the monosulfonic acid of acetyl pyrrole. They did not separate the free sulfonic acid in view of its instability. Even the position of the sulfogroup was not determined. In 1925, B. V. Tronov [4], not cognizant of the work of the Italian authors, again sulfonated α-acetylpyrrole with concentrated sulfuric acid. He separated the barium salt, also corresponding to the monosulfonic acid, as indicated by the barium content. Tronov did not determine the structure of the sulfonic acid obtained. Strangely enough, this sulfoacetyl pyrrole was not included in the IV edition of Beilstein.

In 1935, P. Pratesi obtained an excellent yield of 2,4-dimethyl-5-carbethoxy-3-sulfonic acid from 2,4-dimethyl-5-carbethoxypyrrole by chilling it in a chloroform solution of chlorsulfonic acid. With this reagent, 2,4-dimethyl-3-carbethoxypyrrole resinified. In the sulfonation of 2,4-dimethyl-5-formylpyrrole a side condensation reaction took place with the formation of



The author supposed that he sulfonated a pyrrole derivative for the first time.

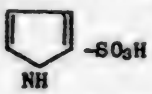
As is evident, all the above-described cases relate only to the sulfonation of pyrrole derivatives with the "stabilizing" groups ($-COCH_3$, $-COOC_2H_5$, $-CHO$). Up to now, pyrrole itself and its homologs have not been sulfonated.

We note that Ciamician and Silber, in their brief report, mention that they attempted the sulfonation of pyrrole with $H_2SO_4$ vapor and observed that a complete resinification did not take place. They expressed the hope that they would be able to report further investigations in the near future. It is evident, however, that their experiments did not lead to positive results.

Our initial experiments on sulfonation with the aid of pyridine-sulfotrioxide indicated that pyrrole is a more acidophobic compound than furan, which we studied earlier, and easily resinifies. But after a series of experiments we succeeded in working out conditions for the reaction which gave highly satisfactory results.

## EXPERIMENTAL

### Pyrrolesulfonic-(2) acid




The reaction was conducted in a solution of the components in dichlorethane. The best yield (about 90%) was obtained by using three molecules of the sulfonating agent for one molecule of pyrrole. For example: 1 g of pyrrole, 6.6 g of pyridine-sulfotrioxide, 5 ml of dichlorethane were heated in a sealed tube in a boiling water bath for 8–10 hours. A dark-brown, caked mass was obtained with a colorless layer of dichlorethane. The reaction mixture was heated with an excess barium carbonate for 30–45 minutes. As a result the dichlorethane and pyridine were removed with the water vapor. If baryta is used, the excess is removed by carbon dioxide gas. After evaporating the filtrate to a small volume and precipitating with alcohol, 3 g of the barium salt were obtained as a white crystalline precipitate, which was purified by a repeated solution in water and precipitation with alcohol. The salt is easily soluble in water, very slightly in alcohol and insoluble in the usual organic solvents.

The sodium and silver salts were obtained by subsequent double decomposition. The latter was difficultly soluble in water and quickly darkened upon storage.

Analyses of the barium, sodium and silver salts indicated that the monosulfonic acid of pyrrole was obtained.

Analysis of the barium salt:

3.844 mg substance: 2.100 mg $BaSO_4$
0.1021 g substance: 0.0085 g $N_2$ (by Kjeldahl method).
Found %: Ba 32.17; N 6.37.
$(C_4H_4O_3NS)_2Ba$. Calculated %: Ba 31.99; N 6.56.

Analysis of the sodium salt:

3.880 mg substance: 1.680 mg $Na_2SO_4$
Found %: Na 14.02.
$C_4H_4O_3NSNa$. Calculated %: Na 13.60.

Analysis of the silver salt:

1.005 mg substance: 0.619 mg $Ag_2SO_4$
Found %: Ag 42.65.
$C_4H_4O_3NSAg$. Calculated %: Ag 42.49.

Pyrrolesulfonic acid was obtained in the free state by treating the barium salt with a calculated quantity of sulfuric acid. It formed hygroscopic crystals, quickly changing in air. It could not be separated in an analytically pure condition.

The structure of the sulfonic acid was determined by oxidizing the barium salt with chromate mixture at 40°. A precipitate of barium sulfate quickly separated and from the filtrate the maleinimide with a m.p. of 92–93° was extracted with ether. The latter was further identified by determining its melting point when mixed with maleinimide obtained from the oxidation of pyrrole by the method of Planchor and Cattadori [6]. From this it is evident that the sulfogroup is situated in the α-position. This was confirmed by oxidizing the barium salt with bromine water. A precipitate separated in the cold; upon washing it with alcohol and ether the dibrommaleinimide with a m.p. of 224–226° was obtained from the solution, as indicated in the literature, and the residue was found to be barium sulfate.

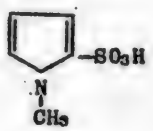
Hydrolysis of the barium salt by hydrochloric acid takes place rather easily and, like furansulfonic-(2) acid, sulfur dioxide gas is evolved.

Reduction by heating in an aqueous solution with 2% sodium amalgam led to the formation of barium sulfite. From the solution a strong base was distilled with the steam, which we have not yet investigated.

By the action of diazotized p-nitroaniline on the barium salt, a precipitation of barium sulfate took place and an orange azoderivative was formed. It is evident that pyrrolesulfonic acid behaves similarly to pyrrolecarboxylic acid, which substitutes the azogroup for the carboxyl under these conditions [7]. Thus, the sulfogroup in the pyrrole nucleus is more mobile than in furan.

It must be noted that pyridine-sulfotrioxide reacts with pyrrole even at a lower temperature. However, the N-derivative then forms. We observed this from the fact that the sulfonation products formed at lower temperatures are characterized by their instability. Azoderivatives of the sulfamino acid type are rather easily hydrolyzed by boiling with barium oxide.

1-Methylpyrrolesulfonic-(2) acid




The original 1-methylpyrrole was obtained by distilling the methyl amine of mucic acid. Boiling point is 114-116°. Methylpyrrole, 1.37 g, was heated with 3 g of pyridine-sulfotrioxide and 5 ml of dichlorethane in a sealed tube at 100° for 8-9 hours. After the usual treatment 2.18 g of the barium salt was obtained (57% of theoretical). White crystals, easily soluble in water, insoluble in organic solvents. Analysis showed that the salt corresponded to the monosulfonic acid.

Analysis of the barium salt:

5.354 mg substance: 2.689 mg $BaSO_4$
4.074 mg substance: 2.035 mg $BaSO_4$
Found %: Ba 29.48, 30.26.
$(C_5H_6O_3NS)_2Ba$. Calculated %: Ba 30.02.

The sulfogroup occupies the α-position. Like the above-described pyrrolesulfonic-(2) acid, upon treating the barium salt with bromine water in the cold a decomposition takes place with the precipitation of barium sulfate and the formation of N-methyldibrommaleinimide with a m.p. of 121°, which corresponds to the data in the literature [8].

2-Methylpyrrolesulfonic-(5) acid

α-Methylpyrrole was obtained according to Yur'ev [9], by passing sylvan over aluminum oxide at 450°. It boiled at 148-149°. For 1 g of methylpyrrole, 5 g of pyridine-sulfotrioxide and 5 ml of dichlorethane were taken. The temperature of the reaction was 100°; the duration was 10 hours. 2 g of the barium salt was obtained, i.e. 54% of theoretical, on a basis of the monosulfonic acid.

Analysis of the barium salt:

4.454 mg substance: 2.303 mg $BaSO_4$
3.728 mg substance: [illegible] mg $BaSO_4$.
Found %: Ba 30.[illegible], 29.9
$(C_5H_6O_3NS)_2Ba$. Calculated %: Ba [illegible]

The salt formed white crystals, easily soluble in water, with difficulty in alcohol. By the action of bromine water a precipitate was obtained, from which by washing with alcohol and

ether the acid-insoluble barium sulfate was obtained. Upon hydrolysis by warming with strong hydrochloric acid, sulfur dioxide gas was evolved. This characteristic undoubtedly indicates the α-position of the sulfogroup.

### 2,4-Dimethylpyrrolesulfonic-(2) acid

2,4-Dimethylpyrrole was obtained from acetoacetic ester according to Fischer and Walach [10]. The treatment was carried out as shown for pyrrole. 2 g of the substance was heated 10 hours at 100° with 10 g of pyridine-sulfotrioxide in 5 ml of dichlorethane. 4.3 g of the barium salt was obtained, which corresponded to a yield of 84%. The salt obtained was of a yellow color. It was easily soluble in water and markedly soluble in alcohol.

By analysis it corresponded to the monosulfonic acid.

Analysis of the barium salt:

4.138 Mg substance: 1.957 mg $BaSO_4$.
2.923 mg substance: 1.409 mg $BaSO_4$
Found %: Ba 27.82, 28.34.
$(C_6H_8O_3NS)_2Ba$. Calculated %: Ba 28.30.

The sulfogroup undoubtedly occupies the α-position. This follows from the fact that the β-position for pyrrole does not sulfonate under our conditions, as will be shown below in the example of 2,5-dimethylpyrrole. Besides, all the reactions of the barium salt of 2,4-dimethylpyrrolesulfonic acid indicate the correspondence to α-pyrrolesulfonic acid: the hydrolysis with hydrochloric acid proceeds without difficulty with the evolution of sulfur dioxide; bromine water in the cold forms a precipitate of barium sulfate.

### 2,5-Dimethylpyrrole

As was shown in the report by Terent'ev and Kazitsina [11], 2,5-dimethylfuran was easily sulfonated in the β-position. The sulfonation of sylvan gave the disulfonic acid. Thiophene, upon sulfonation, yields disulfothiophene with one sulfogroup in the β-position. Concerning α,α'-dimethylpyrrole, we could not sulfonate it using pyridine sulfotrioxide even at 150°. This situation once more confirms, indirectly, that the pyrrole homologs are substituted only in the α-hydrogen atom upon sulfonation. A similar phenomenon was observed in the report of Terent'ev and Tsimbal [12] for indole and its derivatives.

### 1-Sulfophenyl-pyrrolesulfonic-(2) acid

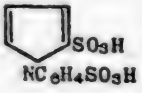
N-Phenylpyrrole was obtained by the method of Yur'ev [13] by passing a mixture of aniline and furan over aluminum oxide at 450-470°. Crystals with a m.p. of 62°.

For 1.43 g of phenylpyrrole, 4.77 g of pyridine-sulfotrioxide (molecular ratio 1:3) and 5 ml of dichlorethane were taken. After heating in a sealed tube for 8 hours at 100° and a subsequent treatment with barium carbonate, 1.1 g of the barium salt was obtained. On the basis of the disulfonic acid, this corresponds to 25% of the theoretical yield.

Analysis of the barium salt:

3.323 mg substance: 1.655 mg $BaSO_4$
5.565 mg substance: 2.814 mg $BaSO_4$
Found %: Ba 31.24, 30.80.
$(C_{10}H_7O_6NS)_2Ba$. Calculated %: Ba 31.32.

The salt is of a white color. Moderate solubility in cold water and better in hot water. Upon treatment with bromine water, a yellowish precipitate was obtained. After washing the precipitate with alcohol and ether the hydrochloric acid-insoluble barium sulfate remained. The hydrolysis proceeded with the formation of sulfur dioxide.



1-o-Tolylpyrrolesulfonic-(2) acid

N-o-Tolylpyrrole was obtained according to Yur'ev [13] from o-tolidine and furan. B.p. 115-117° (13 mm.).

A mixture of 1.3 g of tolylpyrrole, 3.9 g of pyridine-sulfotrioxide (molecular ratio 1:3) and 5 ml of dichlorethane were sealed in a glass tube and heated 8 hours at 100°. By treating the sulfomixture with barium carbonate, 1.15 g of the barium salt was obtained, i.e. 45% of the theoretical, on a basis of the monosulfonic acid.

Analysis of the barium salt:

5.565 mg substance: 2.208 mg $BaSO_4$
3.886 mg substance: 1.513 mg $BaSO_4$.
Found %: Ba 23.35, 22.91.
$(C_{11}H_{10}O_3NS)_2Ba$. Calculated %: Ba 22.53.

White crystals, sparingly soluble in water. Hydrolysis with strong hydrochloric acid took place with evolution of sulfur dioxide and more readily than the previous substance. Bromine water decomposed the salt, after which barium sulfate was found in the precipitate, in line with the solubility of the derivatives in organic solvents.

Thus, by the properties of the sulfoderivatives of phenyl and o-tolylpyrroles it can be positively stated that both contain a sulfogroup in the α-position.

## CONCLUSIONS

The sulfonation of pyrrole and its derivatives were carried out by heating with three times the number of moles of pyridine-sulfotrioxide in a solution of dichlorethane. By this method there were obtained: pyrrolesulfonic-(2) acid, 1-methylpyrrolesulfonic-(2) acid, 2-methylpyrrolesulfonic-(5) acid, 1-sulfophenylpyrrolesulfonic-(2) acid, 2,4-dimethylpyrrolesulfonic-(5) acid, 1-o-tolylpyrrolesulfonic-(2) acid. 2,5-Dimethylpyrrole could not be sulfonated even at a temperature of 150°.

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# DERIVATIVES OF QUINOLINE

## III. MECHANISM OF THE QUINALDINE SYNTHESIS

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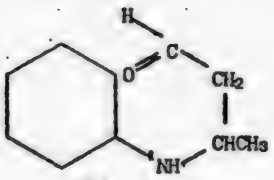
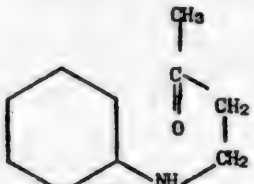
The mechanism of the Skraup and Doebner-Miller reactions and their various modifications have been insufficiently studied, which was observed by us in previous reports [1,2]. These reactions are widely used for the synthesis of quinoline and its derivatives, and it is therefore understandable that a detailed study of their mechanisms would be of definite interest for the theoretical and practical study of nitrogen-containing heterocyclic compounds.

Up to now the fundamental reaction in the Doebner-Miller quinaldine synthesis was believed to be the formation from paraldehyde or acetaldehyde of crotonaldehyde condensed with aniline. The possibility of forming the Schiff base $C_6H_5N{=}CH-CH{=}CHCH_3$ as a kind of intermediate condensation product was refuted by the fact that this compound, after the closure of the cycle, should have yielded lepidine whereas, as is known, the product of the Doebner-Miller synthesis is quinaldine. On this basis, Beyer [3] proposed that an intermediate product is formed by the combination of aniline with croton aldehyde at the double bond, forming β-phenylaminobutyraldehyde (1). Simon [4] extended this assumption to other unsaturated aldehydes and ketones; thus, in the case of methylvinylketone, according to his opinion, methyl-β-phenylaminoethylketone (2) should form:



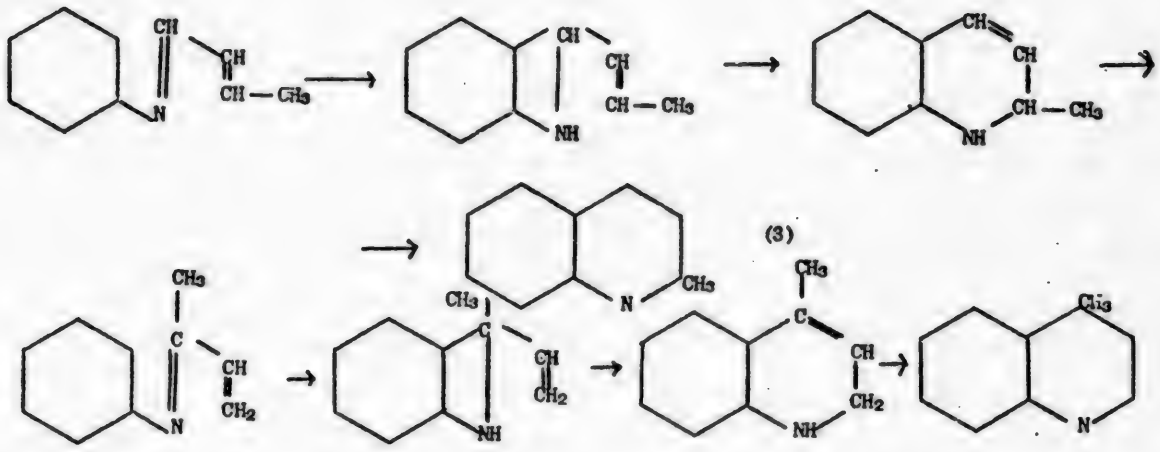

(1)




(2)

The removal of a portion of the water yields a heterocyclic compound. Since the inertness of the aldehyde group in the reaction with the amine is so striking, it was proposed that the corresponding anil was formed with the separation of aniline. This variant was subsequently taken up by Koenigs [5] The Simon mechanism is widely used by chemists at the present time and is reflected in a whole series of textbooks on organic chemistry. The principal inadequacies in the Simon mechanism are first, the absence of experimental proof of the formation of β-phenylaminobutyraldehyde, although it may be formed by other means. Secondly, and most important, according to the Simon mechanism, secondary amines should also yield derivatives of quinoline with acetaldehyde or crotonaldehyde, whereas actually this is not observed.

In 1941, we synthesized, for the first time, the anil of crotonaldehyde, which formed quinaldine upon heating with mineral acids [2], on the basis of which the mechanism for the synthesis of quinaldine from aniline and crotonaldehyde (3) or lepidine from aniline and vinylmethylketone (4) may be presented in the following fashion:



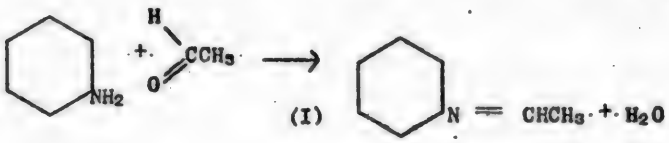
(3)

i.e. the intermediate product is Schiff's base, forming an unstable four-membered ring, which was assumed by Doebner and Miller [6], although they had no crotonylidene aniline.

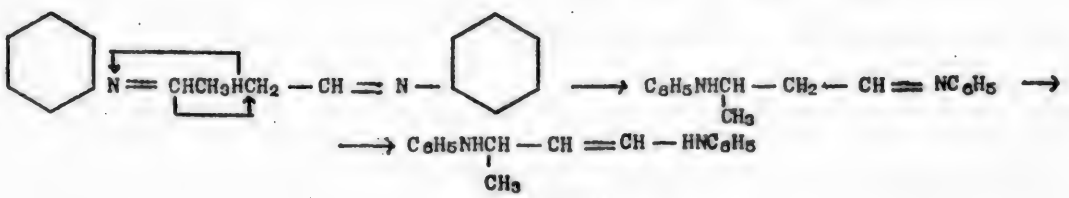
Objections to the proposed mechanism are the lack of proof of the formation of the four-membered, nitrogen-containing ring and the fact that aniline, in the presence of mineral acids, reacts actively and quickly with unsaturated hydrocarbons, which indirectly confirms the Simon mechanism. However, the fact we established that quinaldine is formed from crotonylidene aniline – a reaction widely used even for other aromatic anils [6] – cannot be explained by the Simon mechanism.

At the present time, the supposition that the formation of aldol and consequently crotonylidene aniline in an acid medium is of significance, can hardly be considered competent. More preferably, this formation must be considered as a side reaction and not a fundamental one, as is incorrectly assumed in the chemical literature, especially in textbooks on organic chemistry.

On the basis of data in the literature and work we conducted, the mechanism of the quinaldine synthesis may be fundamentally presented, as we see it, in the following fashion:



(I)



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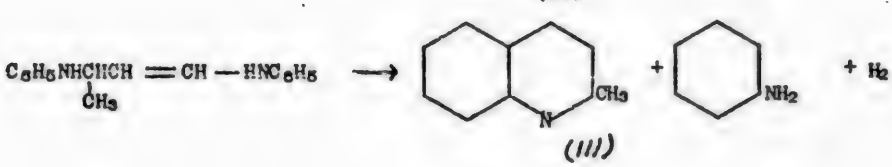

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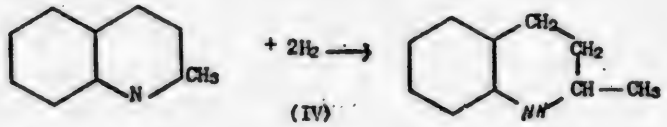

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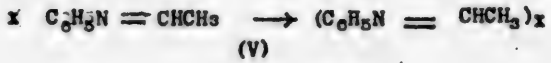

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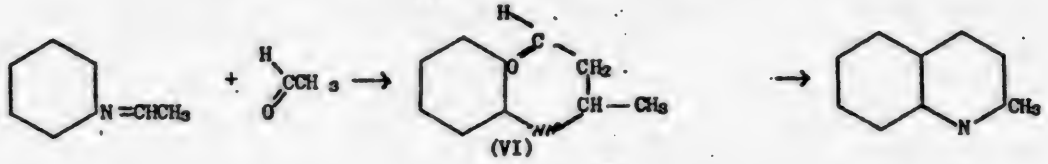

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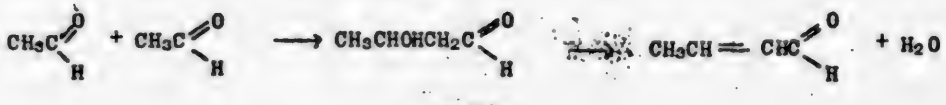

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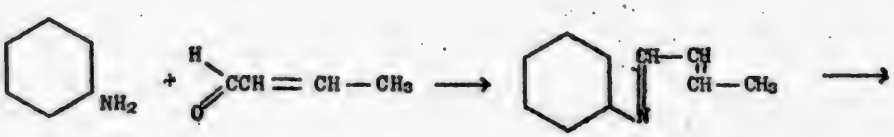

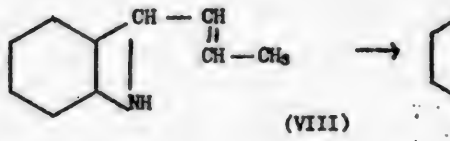

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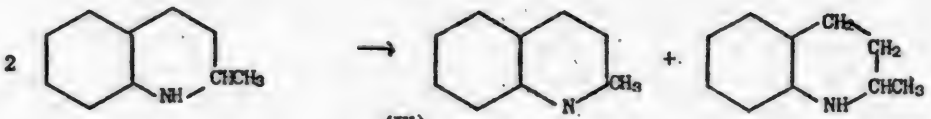

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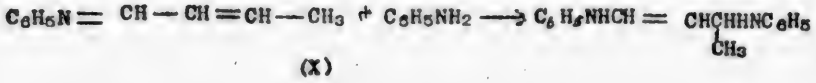
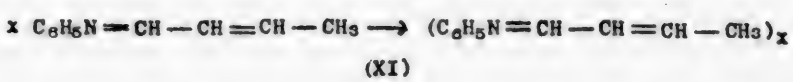


(X)



(XI)

We believe that the principal trend in the Doebner-Miller quinaldine synthesis is the direct reaction between aniline and acetaldehyde with the formation of ethylidene aniline, which is converted into the dimer by a kind of aldol condensation [7], and then, in accordance with the work of W. Meister [8], into the Fikstein-Eibner base. The shift of the double bond in the intermediate reaction product (II) is fully possible, according to the work of M. Turcana [9]

The Ekstein and Eibner base, as is known, is converted to quinaldine, aniline and tetrahydroquinone upon heating [7]. Besides, at a high acidity, the reaction medium in the Doebner-Miller reaction may permit a greater polymerization of the ethylidene aniline with the formation of a resin [10], which is expressed by reaction (V). Reaction (VI) indicates the possibility of forming β-phenylaminobutyraldehyde by another, more probable path than that taken by Beyer and Simon [3,4], and to a certain extent can be taken as a secondary reaction.

The possibility of forming the Eckstein and Eibner base in the Doebner-Miller reaction was first proposed by Miller [11] and in more recent times was noted by N.C.Kozlov [12]. In line with this path of the reaction, the formation of croton aldehyde and its action with aniline must be kept in mind. This is expressed in reactions (VII) - (IX).

The formation of tetrahydroquinaldine by reaction (IX) at the expense of dihydroquinaldine is usually accepted by authors working on the Doebner-Miller synthesis of quinaldine and is confirmed by the presence of 14-16% of tetrahydroquinaldine in the technical product [13]. The instability of dihydroquinaldine, tending to form quinaldine and tetrahydroquinaldine may be explained by quantum resonance. As a result of the reaction, tetrahydroquinaldine is formed in which the benzene nucleus and quinaldine with its variety of structures are preserved.* If the small gain in energy from the presence of the double bond in the pyridine nucleus is neglected, then the process actually leads to a transfer of resonance in benzene to resonance in quinaldine. In this connection, a large energy gain causes reaction (IX) to proceed from left to right, analogous to the conversion of dihydronaphthalene to naphthalene and tetraline [14].

It seems possible to us, that in the presence of excess aniline, the Eibner-Ekstein base is also formed by reaction (X) (1,4 addition) [2] and a resin is partially formed by the diene polymerization reaction of crotonylidene aniline in a kind of chain reaction, similar to the allylidene aniline resins [1,15]. The formation of ethylidene aniline and its subsequent transformation, a basic path of reaction for the quinaldine synthesis, is ascertained by the formation of a considerable quantity of ethylaniline, obtained from its reduction. Ethylaniline was first separated by Doebner and Miller [16] as the nitrosocompound, which was reduced by tin and hydrochloric acid after removal of the ternary base; later by Mills et al. [17] by a slight modification of the Doebner-Miller reaction. n-Butylaniline, formed by the reduction of crotonylidene aniline, was separated only by Mills in the afore-mentioned work. It seems to us that the question of the formation of n-butylaniline and therefore crotonylidene aniline and its relationship to ethylaniline in the Doebner-Miller reaction can be indirectly resolved by conducting the reaction with amines, substituted in the ortho-position relative to the amino group, as for example with mesidine. The impossibility of ring formation in quinoline derivatives permits better and more accurate determinations of the nature of the intermediate products, and therefore the mechanism of the reaction.

As is known, oxidizing agents are not usually applied in the Doebner-Miller quinaldine synthesis, although recently attempts have been made to increase the yield of the synthetic product by oxidation of the tetrahydroderivatives. The yield of quinaldine is usually not increased when nitrobenzene in hydrochloric acid is employed [18], probably because of the large degree of resin formation, but when for example benzidine is employed, the introduction of arsenic acid doubles the yield, as a result of the oxidation of the octahydrobiquinaldine that is formed [13]. By the use of stannic chloride or ferric chloride a 40% yield of lepidine from methyl-β-chlorethylketone [19] was achieved. - By conducting the reaction in a sulfuric acid medium, which increases its resemblance to the Skraup reaction in which, as is known, the application of oxidizing agents is of considerable significance, the action of oxidizing agents will also become more effective. The syntheses of Untermohlen [20], Manske et al. [21], and the syntheses we conducted from ethylene glycol and aromatic amines may serve as examples.

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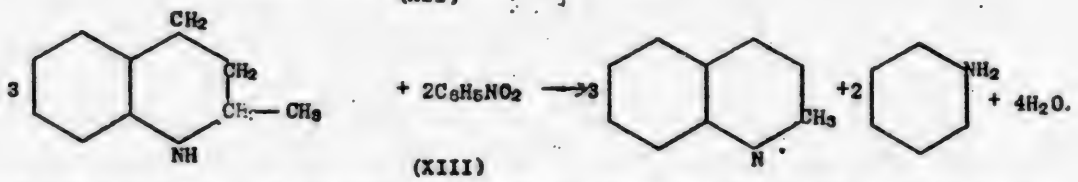
* In quinaldine, there are 10 electrons, forming π-bonds; therefore the number of independent valence structures will be:

$$\frac{10!}{5!6!} = 42 \text{ (forty two).}$$

In the case where nitrobenzene is used, the above schematic equations must be supplemented:

$$C_6H_5NO_2 + 3H_2 \longrightarrow C_6H_5NH_2 + 2H_2O$$

(XII)



(XIII)

i.e., from one standpoint, the hydrogen separating in the reaction combines with the nitrobenzene, decreasing the formation of tetrahydroquinaldine, and from another standpoint, the partial formation of tetrahydroquinaldine by reactions (IV) and (IX) is oxidized to quinaldine. The aniline separating in both cases participates in a reaction similar to the original.

It is understandable that the schematic chart we presented does not pretend to be an exhaustive study of the complex reactions of the quinaldine synthesis. For example, it can be safely stated that the composition of the products of resinification will include the polymerization products of indole and its homologs. This is explained by the fact that o-toluidine gives a considerably smaller yield of quinoline derivatives than p-toluidine, while o-anisidine gives a better yield than p-anisidine [22]. The homologs of indole were separated by us by conducting the reaction under milder conditions and with zinc chloride. The large quantity of resin formed in the usual course of the quinaldine synthesis, and consisting of more than 60% of the yield based on aniline, will always be an obstacle to a detailed investigation of the mechanism of the reaction because of the well-known difficulties connected with the investigation of this resin.

The role of each reaction taking part in the schematic chart presented depends upon its reaction rate, and only by a study of the kinetics of the individual reactions can their significance in the quinaldine synthesis be more accurately shown, although we believe that the basic mechanism of the process has been quite definitely described. Thus, from the characteristics of the quinaldine synthesis which we presented it is evident that it is impossible to carry out the Doebner-Miller reaction, which is specific for acetaldehyde, analogously to the Skraup reaction, as is often done. The latter takes place chiefly because of an unsaturated aldehyde - acrolein - which causes a higher yield of quinoline in comparison with quinaldine, which is only partially formed, due to croton aldehyde. In those cases where by the choice of suitable conditions, unsaturated aldehydes or ketones principally participate in the Doebner-Miller reaction, the yields of the quinaldine preparations are increased. This may be confirmed by a whole series of works [20,23,24].

The difference between the mechanisms of the Doebner-Miller and Skraup reactions is explained by the fact that the latter cannot be used for the synthesis of quinolines substituted in the pyridine nucleus; since fundamentally the Doebner-Miller reaction is a condensation with aldehydes and ketones which proceeds, as we have established, because of the monoethylidene-aniline bases of the immediate products of reaction of acetaldehyde with aniline, while at the same time allylidene anilines immediately form in the Skraup reaction [1], forming heterocyclic compounds.

The mechanism we selected for the quinaldine synthesis, is also confirmed by experiments we conducted, which will be published partially in the near future.

## CONCLUSIONS

1. The Simon mechanism for the quinaldine synthesis is primitive, and is inadequate in relation to the contemporary status of this question.

2. The formation of monoethylidene bases and Eibner-Ekstein bases is considered as being

the principal course of reaction in the quinaldine synthesis of Doebner-Miller. The formation of crotonylidene aniline and its conversion to quinaldine is considered a side reaction in the quinaldine synthesis.

3. It was noted that the Skraup reaction cannot be considered as a special case of the basic version of the Doebner-Miller reaction.

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# DERIVATIVES OF QUINOLINE

## IV. SYNTHESIS OF QUINALDINE AND SEVERAL OF ITS HOMOLOGS FROM AROMATIC AMINES AND ETHYLENE GLYCOL.

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Substituted quinolines are acquiring a greater significance as a result of their application in various fields of industry, principally in the production of dyes, for example, quinophthalones and cyanines, in medicine, in analytical chemistry and for the synthesis of the alkaloids. A wider distribution of the quinoline derivatives is limited by the absence of simple and inexpensive methods for preparing them [1].

At the present time, quinoline and its substitution products in the aromatic nucleus are synthesized by the classical Skraup method [1;2;6], modified by various investigators [3]. Pure preparations with an excellent yield are obtained with boric acid by the Cohn modification [4,6]. The Skraup method, as is known, excludes the possibility of synthesizing quinolines substituted in the pyridine nucleus. The Doebner and Miller reaction [1;5,6] is usually used to accomplish this end, but this, however, is unsuitable for the commercial production of quinoline homologs because of the high volatility of the aldehydes used and in many cases because of the difficulty of obtaining them. The Friedlander synthesis is quite applicable for the formation of the quinoline ring, but is little used, even in the laboratory, because of the complexity of the starting materials, [1,6]. It is therefore understandable that for the commercial synthesis of lepidine and quinaldine, the method of Knorr is used [1,6,7], i.e. the reaction of aniline with an acetoacetic ester, which, although it proceeds in several stages gives pure derivatives with a fairly good yield. Comparatively recently, the synthesis developed by N.C.Kozlov [1;8] for derivatives of quinoline from aromatic amines and acetylene has not found practical application, chiefly because of the inadequate yield; and although the necessity of using solvents and catalysts, together with several other special features considerably lowered the basic superiority of this reaction, it included inexpensive raw materials. As was noted by this author [9], the introduction of oxidizing agents into the reaction did not increase the yield of quinaldine, evidently because of the high degree of resin formation. In recent years, several investigators made use of the direct application of unsaturated aldehydes and ketones for the synthesis of the homologs of quinoline, obtaining high yields [10,11]. These syntheses would be profitable only if the starting materials could be obtained commercially, which was often difficult. The special methods required to obtain them were not justified by the increased yields of the quinoline derivatives. R.Kh. Manske synthesized all the monomethyl-and dimethylhomologs of quinoline, in which out of the 21 dimethylquinolines, 7 were obtained by him for the first time [12].

In the present work are conducted syntheses of quinaldine and several of its methyl homologs from aromatic amines and ethylene glycol, which are easily obtainable and inexpensive raw materials, widely used in different types of industry [13,14]. The inexpensiveness of ethylene glycol results from its application as an anti-freeze liquid in automobile and airplane motors.

The first synthesis of quinaldine from aniline and ethylene glycol was accomplished by

Doebner and Miller [5]. The authors used a smaller quantity of ethylene glycol in comparison with their synthesis from acetaldehyde [5] and an excess of sulfuric acid, which produced considerable resinification. They did not indicate the yield of the quinaldine obtained: according to their method we were able to obtain a yield of 10-12% of the theoretical, based on aniline. Changing the procedure by evaporating the water during the reaction resulted in a yield of 37% of theoretical, which is identical with the classical synthesis of Doebner and Miller from aniline and acetaldehyde or paraldehyde, but is superior to it in the cheapness of the raw materials which are more easily obtained and the convenience of operation, because of the considerably lower volatility of ethylene glycol in comparison with aldehydes.

Our attention was turned to the small yield of o-toluquinaldine - 15% of theoretical. We could find no reference to this question in the literature. Doebner and Miller first obtained o-toluquinaldine, [15], but did not indicate its yield.

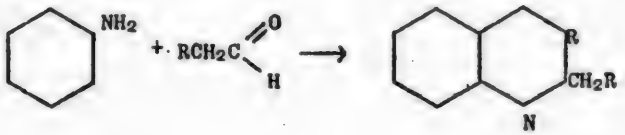
R. Kh. Manske [12] also did not give the yield of o-toluquinaldine, although he cited the yields of almost all the derivatives synthesized. The small yield of o-toluquinaldine may be explained by the immense obstacles encountered, since ring formation in this case is only possible in one direction. We believe that the fundamental reason appears to be the great mobility of the hydrogens of the methyl group in comparison with the hydrogens of the nucleus; this results in the ready formation, from the monoethylidenetoluidine base, of a five-membered indole ring and consequently a great deal of resinification in an acid medium. This consideration is also indirectly confirmed by the fact that upon working with anisidines we observed the reverse phenomenon, that is, o-anisidine gives a better yield than p-anisidine. It is of interest that m-xylidene does not follow the example of o-toluidine, which, it seems, should have been the case. Evidently, three of the substituents - two of them methyl groups in the meta-position, - change the bond to the aromatic nucleus to such a great degree that the hydrogens of the nucleus become more mobile. As one of many examples confirming this phenomenon, the different rates of nitration of benzene, m-xylene and mesitylene [18] may be pointed out, bearing in mind that aminogroups also influence the case we are investigating.

It was established that addition of ferric sulfate or boric acid, successfully used for the synthesis of quinoline [4], does not noticeably affect the yield, which is understandable, if the different mechanisms of these reactions are borne in mind [17]. Although undoubtedly ethylene glycol forms acetaldehyde in a sulfuric acid medium and the fundamental mechanism of the reaction may be assumed to be that described for the Doebner and Miller reaction [17], it is evident that ethylene glycol also has a specific action. Upon conducting the reaction in the absence of oxidizing agents, after reduction of the separated nitrosoamines, we isolated from the 195-220° fraction a base with a m.p. of 207°, forming other derivatives than that expected for ethylaniline. The picrate of the base melted at 221°, the benzene derivative at 171°. Up to now the base has not been further investigated. In this fraction ethylaniline was also found and from the fraction 238-250° was identified tetrahydroquinaldine in the form of a picrate and the benzoyl derivative. We did not find n-butylaniline.

Preliminary experiments established that the reactions for the formation of quinoline derivatives are also characteristic for other α-glycols. Thus, aniline and 1,2-propyleneglycol give 2-ethyl-3-methylquinoline.

In general, the following scheme may be cited:

1. $RCHOHCH_2OH \longrightarrow RCH_2-C(=O)H$

2. 

Instead of aniline, substituted anilines and also diamines may be taken. Thus, benzidine forms biquinaldine, which is of interest in the synthesis of substantive dyes [18].

## EXPERIMENTAL

### Synthesis of quinaldine

Starting materials: aniline b.p. 183-184°, ethylene glycol b.p. 196-197°, nitrobenzene b.p. 209-211°, sulfuric acid sp. g. 1.84.

Experiment 1. In a liter flask are placed 15.5 g of aniline, 10 g of nitrobenzene and 50 g of freshly-distilled ethylene glycol. The mixture is stirred and 35 ml of concentrated sulfuric acid is added with careful stirring, the flask connected to a reflux condenser and heated on an oil bath to gentle boiling, holding it at this point for 5-6 hours. The temperature of the reaction is 145-150°. The mixture is then cooled, water added and the unreacted nitrobenzene steam distilled. The residue is then made alkaline with strong alkali and then the quinaldine and unreacted aniline are steam distilled. The distillate is acidified with 15 ml of concentrated sulfuric acid, cooled to room temperature by adding pieces of ice, and then diazotized to remove the aniline by adding 10 g of sodium nitrite in 50 ml of water. It is subsequently heated on a water bath until the evolution of nitrogen has ceased (formation of phenol), made alkaline with strong alkali and the quinaldine steam distilled. The distillate is extracted with ether, dried with potash, the ether evaporated and the quinaldine distilled.

Boiling point at 760 mm., 237-243°. Yield 4.8 - 5 g. i.e. 22% of the theoretical. The picrate has a b.p. of 190-191°.

Since by the aldehyde method of Doebner-Miller the yield of quinadine is about 40%, we decided to ascertain how completely the aniline reacts in this reaction.

Experiment 2. Up to the distillation of the mixture of quinaldine and unreacted aniline, the experiment is conducted as in the first experiment. The distilled mixture of quinaldine and aniline was extracted with ether, the ether evaporated, and the residue of the base (8.8 g) fractionally distilled. There was obtained:

| | |
|---|---|
| 1st fraction 180-200° | 3.8 g |
| 2nd fraction 235-243° | 4.5 g |
| Residue in the flask | 0.3 g |
| Total | 8.6 g |
| Loss | 0.2 g |

Thus, it was established that about half of the aniline did not enter into the reaction, evidently due to the dilute acid formed from the water separated from the ethylene glycol, which is also in accordance with the mechanism of the quinaldine synthesis [17].

It was therefore considered expedient to carry out the reaction with evaporation of the water formed.

Experiment 3. The procedure is the same as that of the second experiment, but after heating for 3 hours, the water is slowly evaporated during the course of the next 3 hours (a reflux air condenser was substituted for the horizontal water condenser), the temperature being raised slowly to 170°. The amount of nitrobenzene taken was 12 g, the water evaporated was 23 ml.; part of the nitrobenzene was removed with the water, but in very insignificant quantities. Upon increasing the scale of operations it will be expedient to introduce distilled nitrobenzene into the reaction or to use an excess of it. 9.3 g of a mixture of bases was obtained, from which:

| | |
|---|---|
| 1st fraction to 200° | 0.2 g |
| 2nd fraction 200-225° | 2.6 g |
| 3rd fraction 235-243° | 6.0 g |
| residue in the flask | 0.3 g |
| Total | 9.1 g |
| Loss | 0.2 g |

The second fraction consists of quinaldine, the boiling point of which is slightly lowered by the presence of impurities.

$n_D^{24}$ 1.5983; $d_{24}^{24}$ 1.059; instead of $n_D^{20}$ 1.607 and $d_4^{20}$ 1.059 for quinaldine.

The picrate has a m.p. of 190°, the double salt with mercuric chloride, 165°.

The third fraction – quinaldine; $n_D^{24}$ 1.6997, $d_4^{20}$ 1.0610. The picrate has a melting point of 191°, the double salt with mercuric chloride, a melting point of 166°, the quinophthalone a m.p. of 233°.

Thus by carrying out the reaction with evaporation of water, 8.6 g of quinaldine were obtained, i.e. 37% of the theoretical yield.

Experiment 4. The conditions were similar to the first experiment, but the water was evaporated as in the third experiment. The mixture of quinaldine and unreacted aniline was diazotized. Quinaldine separated as in the first experiment. 8.5 g of quinaldine obtained with a b.p. of 245–248° at 750 mm. The yield was 37% of theoretical. The picrate had a melting point of 190°, the double salt with mercuric chloride, a m.p. of 166°, the quinophthalone a m.p. of 233°.

$n_D^{20}$ 1.610; $d_{20}^{20}$ 1.060.

Analysis for nitrogen by the Dumas method.

0.1143 g substance: 10.3 ml $N_2$ (23°, 750 mm.)
Found %: N 9.97.
$C_{10}H_9N$. Calculated %: N 9.79.

In separate experiments it was established that aniline was completely consumed in the aldehyde synthesis of Doebner and Miller. Thus 60% of the aniline taken had evidently resinified.

One of the advantages of working with ethylene glycol in a sulfuric acid medium was the comparatively rapid steam distillation of the base from the alkaline medium. In our experiments the distillation was completed about twice as fast, i.e. the quantity of distillate upon completion of distillation was one half as much as when the distillation took place from an alkaline medium, formed by the neutralization of the hydrochloride of the base under the conditions of the aldehyde synthesis of Doebner and Miller.

## Synthesis of p-toluquinaldine

Experiment 5. 18 g of p-toluidine, 15 g of p-nitrotoluene, 50 g of ethylene glycol and 34 ml of sulfuric acid were taken for the reaction. The synthesis was conducted as described in the fourth experiment.

After evaporation of the ether, 7.9 g of p-toluquinaldine was obtained, i.e. 30% of the theoretical, in the form of a partially crystallized oil. After vacuum distillation, from the fraction with a b.p. of 128 –133° (12 mm.) there was formed upon cooling a solid mass of crystals with a characteristic anise odor, which after recrystallization from petroleum ether, melted at 60°. The picrate had a m.p. of 179°, the double mercuric salt a m.p. of 189°, the quinophthalone a m.p. of 235°.

Analyses for nitrogen by the Dumas Method

0.1335 g substance: 10.6 ml $N_2$ (21°, 748 mm)
Found %: N 8.95.
$C_{11}H_{11}N$. Calculated %: N 8.90

## Synthesis of o-toluquinaldine

Experiment 6. 18 g of o-toluidine, 15 g of o-nitrotoluene, 50 g of ethylene glycol and 34 ml of sulfuric acid were taken for the reaction. The synthesis was conducted as described in the fourth experiment. The yield of o-toluquinaldine with a b.p. of 245–252° was 4.0 g, which was 15.1% of the theoretical. The picrate had a m.p. of 179°, the double mercuric salt, a m.p. of 195°.

$n_D^{26}$ 1.601; $d_{24}^{24}$ 1.043.

Analysis for nitrogen by the Dumas' Method.

0.1050 g substance: 8.4 ml $N_2$ (22°, 759 mm).
Found %: N 9.00
$C_{11}H_{13}N$. Calculated %: N 8.90.

Synthesis of 2,6,8-trimethylquinoline

Experiment 7. 20.2 g of m-xylylene (1,3-dimethyl-4-amino-benzene), 15 g of nitrobenzene, 50 g of ethylene glycol and 34 ml of sulfuric acid were taken for the reaction.

The synthesis was conducted as described in the fourth experiment. After evaporation of the ether, 7.7 g of 2,6,8-trimethylquinoline was obtained (i.e. 27% of the theoretical) in a liquid form. After distillation under vacuum at 260° (719 mm), it was obtained in a crystalline condition. Upon recrystallization from dilute alcohol it gave a m.p. of 45–46°.

The somewhat smaller yield compared with that earlier obtained by the Doebner-Miller reaction [10] resulted from the incompletely successful application of the oxidizing agent, nitrobenzene, since 1,3-dimethyl-4-nitrobenzene was not available. The picrate had a m.p. of 185°.

Analysis for nitrogen by the Dumas' method:
0.1725 g substance: 12.9 ml $N_2$ (22°, 750 mm.).
Found %: N 8.32.
$C_{12}H_{13}N$. Calculated %: N 8.19.

Increasing the time of heating in the syntheses described does not produce better yields.

The student, L.I.Kurmoiarova participated in this work.

## CONCLUSIONS

1. Quinaldine, o- and p-toluquinaldine and 2,6,8-trimethylquinoline were synthesized from aromatic amines and ethylene glycol in a sulfuric acid medium by the use of oxidizing agents, analogous to the synthesis of quinoline from aniline and glycerine by the Skraup reaction. The yield of quinaldine was 37% of theoretical.

2. The reactions of aromatic amines with ethylene glycol may be considered as a basis for a new, commercially feasible method for the synthesis of quinoline homologs from aromatic amines and α-glycols, and is of practical and theoretical interest.

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# SOME DERIVATIVES OF BENZOTRIAZOLE - II.

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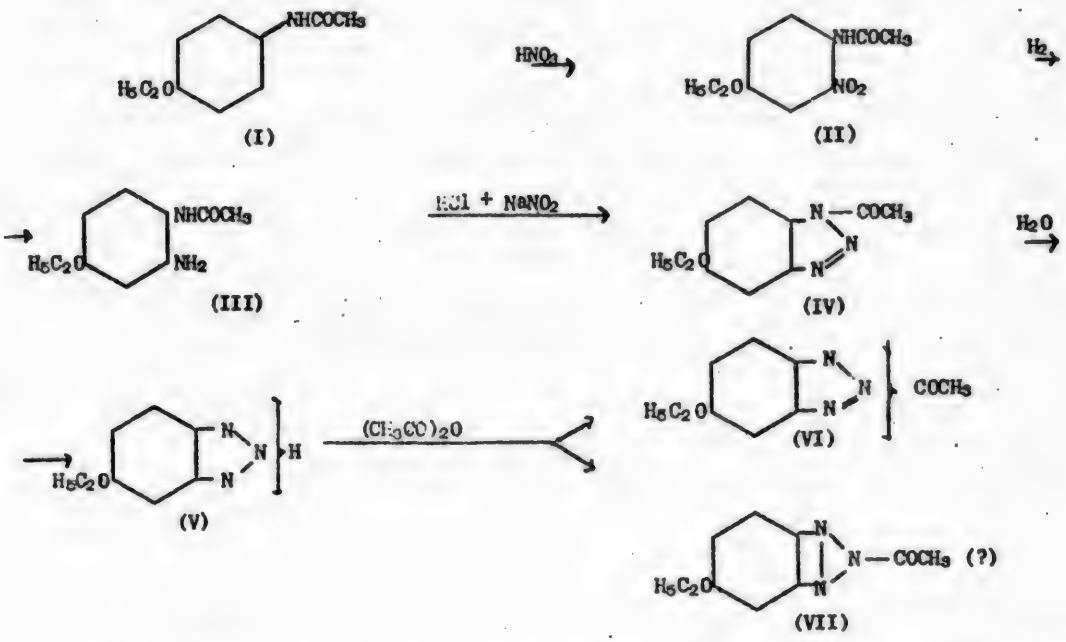
In a previous paper [1], three isomeric acetyl-5-methoxy-benzotriazoles were discussed. In the course of this work we obtained two higher homologs of the above isomers. We obtained acetyl--5-ethoxybenzotriazole from p-acetphenetidine (phenacetin) by nitrating it and by subsequent operations, described below.



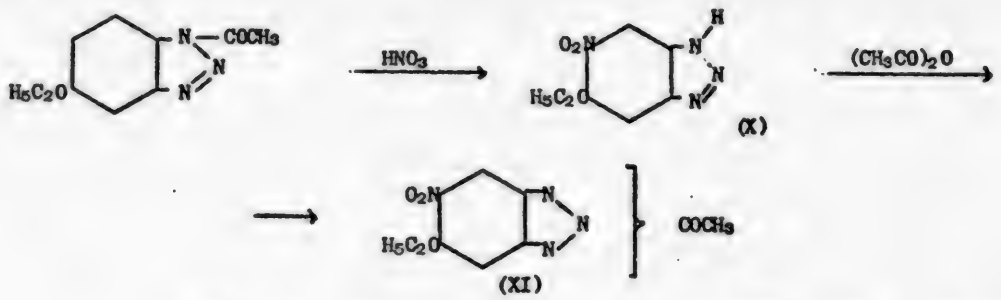

The chart presented permits us to believe that 1-acetyl-5-ethoxy-benzotriazole (IV) was obtained. In this regard, we consider that by the presence of a substituent in the aromatic nucleus (in the given case, the ethoxy group), the position of a substituent in the triazole ring becomes more stable [2].

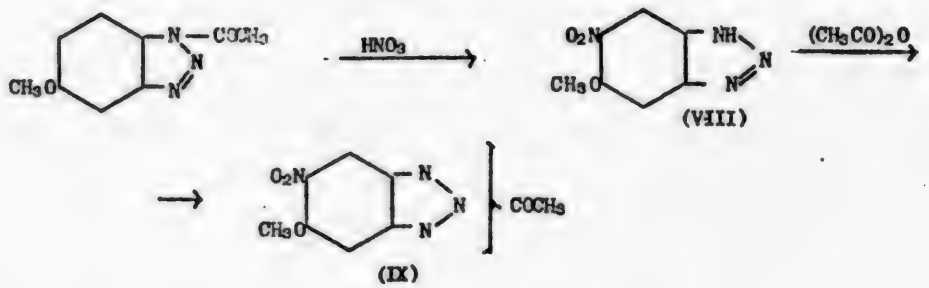
1-Acetyl-5-ethoxybenzotriazole (IV) is a light, rose-colored, crystalline product with a m.p. of 134-136°. Upon hydrolysis there is obtained a white crystalline product - 5-ethoxybenzotriazole with a m.p of 113-115° (V). Upon acetylizing the latter, a white crystalline product is obtained, which upon analysis was shown to be acetylethoxybenzotriazole, but with a m.p. of 90-92°. To demonstrate the structure of this isomer of acetylethoxybenzotriazole (position of the acetyl group) it would be necessary to carry out the synthesis from m-acetphenetidine, as we did for the demonstration of the position of the acetyl group in acetylmethoxybenzotriazole [1]. Time and conditions of operation did not permit us to do this. However, we may consider the isomer in which the acetyl group is found in position 2 (VII). The fact that 2-acetyl-5-methoxybenzotriazole is

obtained by the acetylization of 5-methoxybenzotriazole leads to the postulation that the same occurs upon acetylization of 5-ethoxybenzotriazole. This postulation is to a certain degree confirmed by the melting point of the derivatives obtained:

| | | |
|---|---|---|
| 1-acetyl-5-methoxybenzotriazole<br>140 - 142° | 5-methoxybenzotriazole<br>124 - 126° | 2-acetyl-5-methoxybenzotriazole<br>94 - 96° |
| 1-acetyl-5-ethoxybenzotriazole<br>134 - 136° | 5-ethoxybenzotriazole<br>113 - 115° | 2-acetyl-5-ethoxybenzotriazole<br>90 - 92° |

In further work on the nitration of 1-acetyl-5-methoxybenzotriazole and 1-acetyl-5-ethoxybenzotriazole (see below), the acetyl group was hydrolyzed under the conditions of our experiment and 5-methoxy and 5-ethoxy-6-nitrobenzotriazole were obtained. Upon acetylation of these compounds, acetylalkoxynitrobenzotriazoles were obtained, in which the position of the acetyl group was not determined.




## EXPERIMENTAL

By the nitration of acetphenetidine with weak nitric acid, according to the method described for acetanisidine [1], we obtained 3-nitro-4-acetaminophenetol [3] (II). The derivative obtained is reduced in a neutral medium [1] to the corresponding amine.

### 3-Amino-4-acetaminophenetole (III)

Into a triple-necked flask furnished with a stirrer and thermometer were added 300 ml of water and 10 g of sodium chloride, the solution heated to 80-90° and 90 g of iron filings added with stirring. Then, at the above temperature, 31 g of 3-nitroacetaminophenetole was added in small increments. The water bath was brought to boiling and the reaction continued with mixing for another 2.5 hours. Upon completion of the reaction, the sediment was filtered through a Buchner funnel and twice extracted with hot water. The filtrate and wash water were combined and evaporated under vacuum to one third its volume. A precipitate settled out weighing 25 g; yield 92-93%.

Upon crystallization from water there are obtained light-gray shiny crystals with a m.p.

of 138–139°. They are soluble in the cold in acetone, partially in alcohol and chloroform. Upon heating the crystals dissolve easily in water, alcohol, chloroform and ethyl acetate, but do not dissolve in benzene.

Found %: C 61.96; H 7.11; N 14.31.
$C_{10}H_{14}O_2N_2$. Calculated %: C 61.85; H 7.21; N 14.4[illegible]

1-Acetyl-5-ethoxybenzotriazole (IV)

38 g of 3-amino-4-acetaminophenetole were dissolved in dilute hydrochloric acid (54 ml of 27% hydrochloric acid in 500 ml of water), and the solution cooled to -2°. At this temperature, but not higher than 5° was gradually added a concentrated aqueous solution of 14.6 g of sodium nitrite. The precipitate which formed was filtered by suction and washed with cold water. The dried product weighed 38.5 g (yield 96%). It was soluble at room temperature in acetone, ethyl acetate, benzene and dichlorethane. 1-Acetyl-5-methoxybenzotriazole was soluble with heating in alcohol and petroleum ether. The substance was crystallized from alcohol and had a m.p. of 134–136°.

Found %: C 58.41; H 5.43; N 20.46.
$C_{10}H_{11}O_2N_3$. Calculated %: C 58.53; H 5.36; N 20.48.

5-Ethoxybenzotriazole (V)

10 g of 1-acetyl-5-ethoxybenzotriazole were heated in a Babo funnel under a reflux condenser for 10 hours with 60 ml of 50% acetic acid. The clear, cooled solution was neutralized with bicarbonate to a weakly acid reaction, the precipitate filtered by suction, washed with cold water and dried. Its weight was 8.7 g.

Ethoxybenzotriazole is soluble in the cold in alcohol, acetone, ethyl acetate and chloroform. It is also soluble in hot water and hot benzene. Upon crystallization from benzene it gives colorless crystals, m.p. 113–115°.

Found %: N 25.96.
$C_8H_9ON_3$. Calculated %: N 25.76.

2(?)-Acetyl-5-ethoxybenzotriazole (VII)

4 g of 5-ethoxybenzotriazole, obtained as described above, was heated on a Babo funnel with a reflux condenser in 24 ml of acetic anhydride for 4 hours. The solution obtained was poured into cold water; the precipitate which separated was filtered by suction, washed with water and dried. The yield was almost theoretical. It was soluble in the cold in acetone, ethyl acetate, benzene and upon warming in 70% alcohol. The 2(?)-acetyl-5-ethoxybenzotriazole crystallized from alcohol is obtained as a white crystalline product, m.p. 90–92°.

Found %: C 58.46; H 5.33; N 20.54.
$C_{10}H_{11}O_2N_3$. Calculated %: C 58.53; H 5.36; N 20.48.

5-Methoxy-6-nitrobenzotriazole (VIII)

Into a triple-necked flask, furnished with a stirrer, dropping funnel and thermometer, were introduced 125 ml of concentrated sulfuric acid and then gradually, stirring with the mechanical stirrer, 24 g of 1-acetyl-5-methoxybenzotriazole. To the solution obtained, cooled to -5°, was added the nitrating mixture (25 g of nitric acid, sp. g. 1.35 and 30 ml of concentrated sulfuric acid). Upon completion of the nitration the temperature of the reaction was raised to 50–55°. The mixing was continued another 3 hours. The clear solution obtained was poured onto ice, the precipitate which separated was filtered by suction, and well washed with water. The weight of the obtained product was 25 g. It was very slightly soluble in hot water, insoluble in hot benzene, ethyl acetate, dichlorethane; soluble in hot alcohol, acetone. In alkalies, ammonium hydroxide and sodium carbonate it dissolved, giving a yellowish-green solution. The precipitated potassium salt was of a canary-yellow color and dissolved in hot water. After crystallization from strong alcohol it was obtained as shiny, light green crystals, m.p. 233–234°.

Found %: N 28.72.
$C_7H_6O_4N_4$. Calculated %: N 28.86.

### 5-Methoxy-6-nitroacetylbenzotriazole (IX)

10 g of 5-methoxy-6-nitrobenzotriazole was heated under a reflux condenser on a Babo funnel in 60 ml of acetic anhydride for 5 hours. The clear solution was poured into ice water, the precipitate which then separated was filtered by suction, washed with water and dried. An almost theoretical yield was obtained. It was soluble in the cold in dichlorethane, chloroform and ethyl acetate. Upon heating it dissolved in acetone and with much difficulty in alcohol. After crystallization from a mixture of dichlorethane with alcohol (1:3) crystals were obtained with a very light greenish cast, m.p. 191 -193°.

| | | | |
|---|---|---|---|
| | Found %: | N 23.50; | $CH_3CO$ 18.74; |
| $C_9H_8O_4N_4$: | Calculated %: | N 23.73; | $CH_3CO$ 18.22. |

### 5-Ethoxy-6-nitrobenzotriazole (X)

The substance was obtained by a method identical to that of 5-methoxy-6-nitrobenzotriazole (VIII). The yield of the nitroderivative was 90% of the theoretical. It was insoluble in hot chloroform and ethyl acetate. It was difficultly soluble in hot acetone and alcohol. After crystallization from alcohol it was obtained as light-greenish crystals, m.p. 197-199°.

| | | |
|---|---|---|
| | Found %: | N 27.14. |
| $C_8H_8O_4N_4$. | Calculated %: | N 26.92. |

### 5-Ethoxy-6-nitroacetylbenzotriazole (XI)

5-Ethoxy-6-nitroacetylbenzotriazole was obtained by acetylization with acetic anhydride by the same method as for 5-methoxy-6-nitroacetylbenzotriazole. The yield was almost theoretical. The product was soluble in chloroform, acetone, dichlorethane at room temperature. Upon heating it also dissolved in ethyl acetate, benzene, with more difficulty in alcohol. It was insoluble in petroleum ether and ligroin. Recrystallized from a mixture of alcohol and dichlorethane, it gave greenish crystals, m.p. 167-169°.

| | | | |
|---|---|---|---|
| | Found %: | N 22.05; | $CH_3CO$ 17.55. |
| $C_{10}H_{10}O_4N_4$: | Calculated %: | N 22.4; | $CH_3CO$ 17.20. |

## CONCLUSIONS

1. Two isomers of acetylethoxybenzotriazole were obtained. The structure of one of these was shown by synthesizing it from acetphenetidine. The structure of the second isomer was adduced.

2. The products of the nitration and subsequent acetylization of 1-acetyl-5-methoxy- and 1-acetyl-5-ethoxybenzotriazole were obtained.

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# CHEMICAL STRUCTURE AND PARASITIC ACTIVITY

## IX. ISOMERIC CHLORO-9-AMINOACRIDINE; QUINOID STRUCTURE AND ANTI-PLASMODIUM ACTIVITY

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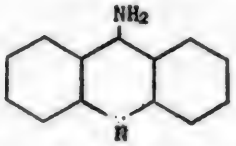
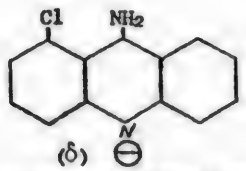
Results of previous studies [1] on the connection between anti-malarial activity and the position of the halide in a series of chlor-isomers of meso-diethylamino-δ-pentylaminoacridines indicated that the activity was very dependent on the location of the halide in the 1 and 3 positions of the acridine nucleus and correspondingly a practical absence of activity in compounds where the halide is located in the 2 and 4 positions; for a complete picture, corresponding acridine compounds not containing substituents in the nucleus were investigated, and also indicated the absence of activity.

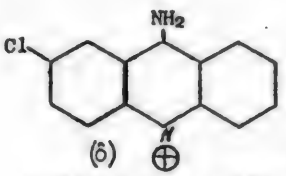
This series of compounds may be considered as derivatives of a basic group, which in the given case is 9-amino-acridine:



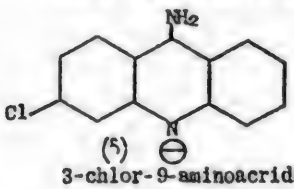
Then the corresponding compounds previously studied [1] are the derivatives:



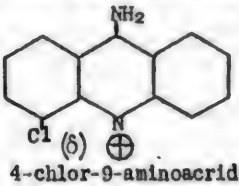
1-chlor-9-aminoacridine



2-chlor-9-aminoacridine



3-chlor-9-aminoacridine



4-chlor-9-aminoacridine

These chlor-isomeric 9-aminoacridines are basic "stem" types of those groups, in which after dialkylaminoalkylization, the 9 amino groups with side chains of the same structure and

composition show quite different antiplasmodial properties. Therefore, interest was raised in these stem substances as possible basic carriers of properties causing this surprising differentiation in biological activity, paralleling the above-mentioned variation in the position of the haloid.

First of all it seemed necessary to compare the relative strength of these compounds as bases. Solutions of these five bases in 5% alcohol were prepared of equal molarity, and their specific electroconductivity at 25° measured. The results obtained are placed in the first column of figures in Table 1. After a period of time, the specific electroconductivity at the same temperature of these solutions, kept in the old vessels (same glass), were again measured; The results of the second measurement are placed in the second column.

TABLE 1

Specific Electroconductivity of Five Aminoacridines at 25°

| | | | |
|---|---|---|---|
| No. 1 | 1-chlor-9-aminoacridine ..... | 0.000021162 | 0.000035582 |
| No. 2 | 2-chlor-9-aminoacridine ..... | 0.000024052 | 0.000043832 |
| No. 3 | 3-chlor-9-aminoacridine ..... | 0.000031682 | 0.000045462 |
| No. 4 | 4-chlor-9-aminoacridine ..... | 0.000020752 | 0.000040912 |
| No. 5 | 9-aminoacridine ..... | 0.000052482 | New solution was prepared |

From these figures (Table 1) it is evident that the strongest base is 9-aminoacridine, not containing a haloid in the nucleus. The presence of a haloid in the 1 position lowers the basicity of the aminoacridine. By moving the haloid from the base center - 9-amino-group - the basicity of the 2- and 3-chloraminoacridines increases and decreases once more upon approach of the haloid to the second base center - to the cyclo nitrogen of the acridine nucleus at the 4-chlor-isomer.

The electroconductivity determinations were carried out by M.M. Yakshin and V.M.Ezuchevska, to whom the authors here express grateful appreciation.

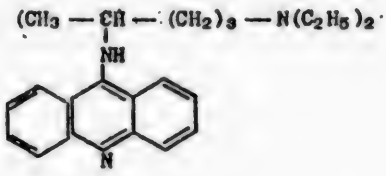
The isomeric chloraminoacridines obtained are stem substances of the antimalarial compounds previously described [1] and served as means to establish new experimental data, which we believe is useful to some degree in the evaluation of the "quinoid principle" of the action of antimalarial compounds, propounded in 1942 by F. Schonhofer [2].

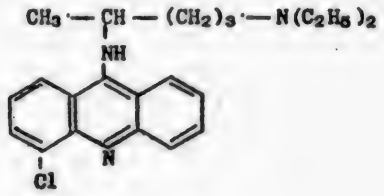
On the basis of the adjacent locations of the active substituents in the 4,8 positions of quinoline and 9 acridine in antimalarial compounds of these classes, which (positions) are ortho- or para to the cyclic nitrogen, the author believes that the action of these substances is related to the quinoid structure originating from the derivatives of, for example, 6-methoxy-8-aminoquinoline as a result of oxidizing processes in the living organism, and from derivatives of 4-aminoquino- and 9-aminoacridine as a result of tautomerisms and rearrangements within the quinolone- and acridone-imino structures. One of the arguments which the author presents in defense of his quinoid theory is the fact that there is a loss in activity as a result of the acylation of the secondary aminogroup, by which the side chain is connected to the nucleus. Because of its hydrogen atom, this group undergoes a tautomeric transformation, the result of which is a rearrangement of the substance into the quinoid form and evidently in conjunction with this the hydrolytic cleavage of the side chain is simplified.

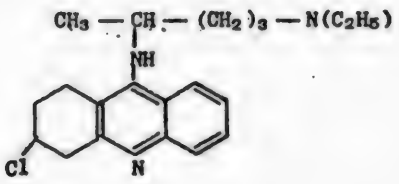
A natural outcome of this idea is the necessity to admit that the quinoid structure should, in large degree, be present in substances with a large amount of activity and that in groups structurally of the same type, satisfactorily constructed so as to make possible its rearrangement into the acridone-imino structure, the activity should be differentiated by the degree of ease of their rearrangement into the quinoid structure.

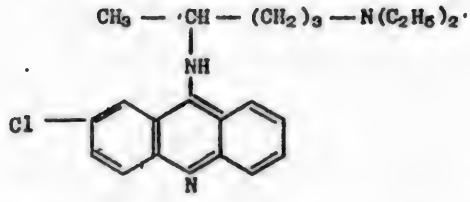
To test this postulation, we turned our attention to the structurally similar type of compounds of the acridine series, which had been previously described by us, [1]. Several

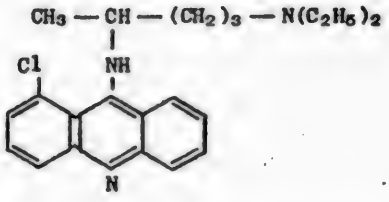
representatives of this group were obtained by us for the first time, others were synthesized for the purpose of obtaining data on their activity. These chlor-isomeric derivatives of 9-aminoacridine and their analogs, not containing chlorine:





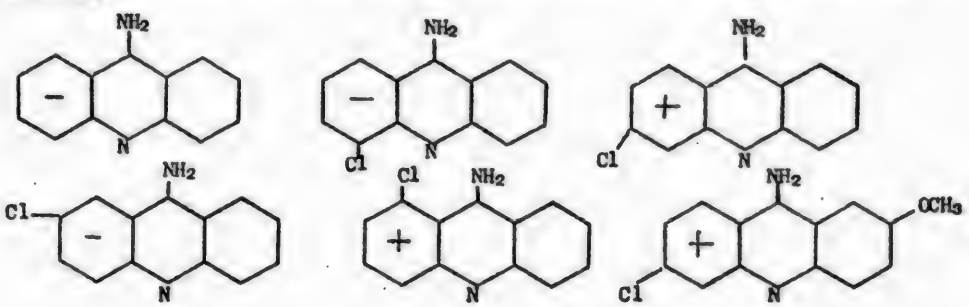






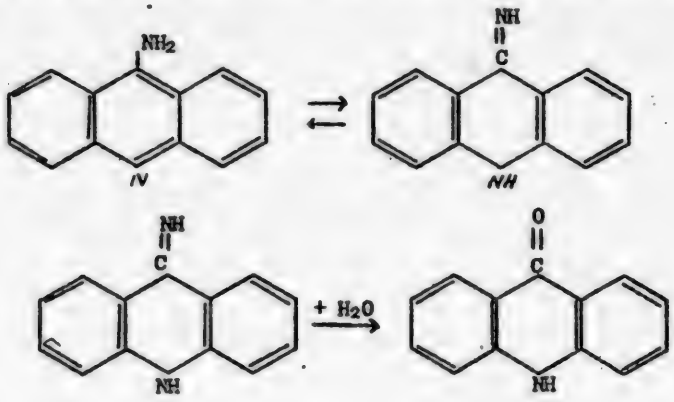
are suitable for the verification of the "quinoid activity" group. From the point of view of structure all the representatives of the group meet the requirement of the presence of a free hydrogen atom capable of tautomeric conversion, conditions for the formation of the quinoid structure. On the other hand, they showed a sharp difference in antimalarial activity. Thus, on the basis of Schonhofer's "quinoid hypothesis" it seemed fully probable that the different positions of the haloid in these compounds cause varying mobility of the active hydrogen of the secondary amino group, and that consequently, in compounds of greater biological activity the degree of rearrangement into the quinoid structure would be correspondingly higher.

For the experimental verification of this postulation we selected the measurement of the relative rate of reaction of these compounds in the quinoid form upon direct hydrolysis. The difficulty of collecting the products of hydrolysis at the time of the reaction and the almost complete identity of the course of this reaction, not with 9-aminoalkylized acridines, but with their "stem substances" were reasons why this rate of reaction in the quinoid form was accordingly measured for four chlor-isomers of 9-aminoacridines, their analog not containing chlorine, and a methoxyl derivative, added to obtain the complete picture. It must be noted that in this series of amino acridines



the dialkylaminoalkylized derivatives of the members of the series, marked with a plus, are highly effective substances, and correspondingly, those marked with a minus are substances with very small or completely absent activity.

The method we selected was as follows: equal weights of the substances were carefully boiled with a solution of alkali and under the same conditions a second portion was determined for nitrogen by the Kjeldahl method. The rate of separation of ammonia was conveniently controlled by back titrating with acid using an indicator, the separation of $NH_3$ taking place according to the reaction.




The results obtained draw a very clear picture: under equal conditions the greatest amount of ammonia was separated from 9-aminoacridine, not containing substituents; next is the chlor-isomer with the haloid in a position closest to the cyclic nitrogen, and the separation of ammonia decreases further as the haloid is moved farther away from the cyclic nitrogen; a peculiarity in this group is that the methoxyl analog releases a relatively small amount of ammonia (see Table 2).

These figures seem to disclaim the quinoid hypothesis of anti-plasmodial activity propounded by Schonhofer.

TABLE 2

Results of the Determination of the Relative Rates of Hydrolysis of Isomers of Chloraminoacridines, their Analog not Containing Chlorine, and 2-Methoxy-6-chlor-9-aminoacridine.*

| Substance | Weight | Amount N/10 HCl used for the neutralization of $NH_3$, distilled with 100, 150 and 200 ml water | | |
|---|---|---|---|---|
| | | 100 | 150 | 200 |
| 1-Chlor-9-aminoacridine | 0.1005 | 3.9 | 5.5 | 6.3 |
| | 0.1000 | 4.2 | 5.8 | 6.4 |
| 2-Chlor-9-aminoacridine | 0.1015 | 3.4 | 4.8 | 5.4 |
| | 0.1008 | 3.4 | 4.9 | 5.6 |
| | 0.1006 | 2.9 | 4.0 | 4.5 |
| 3-Chlor-9-aminoacridine | 0.1010 | 7.5 | 10.0 | 11.4 |
| | 0.1001 | 9.4 | 12.2 | 14.0 |
| 4-Chlor-9-aminoacridine | 0.1007 | 11.3 | 17.0 | 19.2 |
| | 0.1003 | 12.6 | 19.0 | 22.6 |
| 9-Aminoacridine | 0.1006 | 17.0 | 25.1 | 29.4 |
| | 0.1000 | 15.0 | 22.6 | 26.7 |
| 2-Methoxy-6-chlor-9-aminoacridine | 0.1000 | — | — | 2.0 |
| | 0.0985 | 1.5 | 1.6 | 1.7 |

* The small deviation in the figures for 1-chlor-9-aminoacridine may be explained by the presence of a slight admixture of the 3-chlorisomer, extremely difficult to separate.

The data presented here are based on the postulation of rearrangement of 9-aminoacridine derivatives to the acridone-imino tautomeric form upon hydrolysis, while at the same time the possibility is admitted of the separation of ammonia upon rearrangement to the benzoid form. However, the work of A.Albert and B. Ritchije [3] supports our interpretation, and shows that in a large number of reactions 9-(5)-aminoacridines rearrange into the acridone-imino form (negative reactions with aldehydes, with diazotization; formation of 10-N-methylacridoniimines upon methylation, etc.). The interpretation of A.M.Grigorovski on the structure of the diacetyl derivative of 9-aminoacridine as a derivative of the imino form also serves as indirect proof of our contention.

## EXPERIMENTAL

The method for carrying out the hydrolytic decomposition of the isomers of chlor-9-aminoacridones into the corresponding isomers of chloracridone and ammonia is as follows: equal weights of the chlor-isomers are heated under identical conditions with concentrated alkali in a round-bottomed flask of 1 liter volume, furnished with a still head and fitted with a tube for introducing the sample into a boiling solution of sodium hydroxide.

A method for the rapid introduction of the sample is the following. The sample was placed into a foil, the foil was folded up into a package and thrown into the boiling alkali, immediately after which the opening in the tube was securely covered with a rubber stopper. The foil was quickly dissolved in the boiling alkali, permitting an even decomposition of the substance. By means of the still head, the flask was connected to an inclined condenser and a receiver for the distilled ammonia. For the absorption of the ammonia 20 ml of water and 2 drops of methyl red were placed in the receiver and the amount of $NH_3$ passing into the vessel was determined during the distillation by titration with a solution of hydrochloric acid from a burette placed over the receiver.

The sample of material to be hydrolyzed was added to the boiling solution of alkali in order to maintain even temperature conditions from the beginning of the experiment.

1-Chlor-9-aminoacridine, m.p. 267°, 2-Chlor-9-aminoacridine, m.p. 277°, 3-chlor-9-aminoacridine, m.p. 270°, 4-chlor-9-aminoacridine, m.p. 227°, and 9-aminoacridine, m.p. 235°, were prepared by the action of the corresponding isomers of chlor-9-phenoxyacridines and 9-phenoxyacridine with ammonium chloride and phenol [5]; the preparation of these compounds by the action of dichloracridines in phenol with ammonium carbonate was described simultaneously with our work by A. Albert and W. Gledhill [6]; the melting points of the dichloracridine isomers carried out by the English authors coincide with that described above. The preparation of 2-methoxy-6-chlor-9-aminoacridine, m.p. 274°, necessary for our model experiments was obtained from M.P. Gerchuka, to whom we express sincere appreciation.

1. Model Experiments on the Hydrolytic Cleavage of the Aminogroup using 2-Methoxy-6-chlor-9-aminoacridine.

300 ml of water and 100 ml of a 43% solution of sodium hydroxide were heated in a liter flask with a still head and a wide glass tube for introducing the sample. When the water began to distil, 0.2004 g of 2-methoxy-6-chlor-9-aminoacridine contained in a folded foil was added to the boiling alkali through the glass tube and the tube immediately stoppered. The foil quickly dissolved, the substance scattered to the surface of the boiling liquid and while boiling was flung against the wall of the flask, which made uncertain the complete reaction of all the material taken. The experiment was continued until a considerable portion of the volume of the solution was distilled into the receiver and was stopped when a small amount of liquid was left in the flask. The distilled ammonia was neutralized with several drops of N/20 HCl in the presence of methyl red. Since about 15 ml of acid of this concentration was required by calculation to react completely with the ammonia and since the conditions of the reaction were not favorable because the reacting substance was not in solution, hydrolysis experiments in a water-alcohol medium were carried out to verify the results of the first experiment.

2. Hydrolysis Experiments for 2-Methoxy-6-chlor-9-aminoacridine with Water-alcohol Solutions of Alkali.

a) 0.2 g of the substance was dissolved in 100 ml of alcohol, 45 ml of a 43% solution of sodium hydroxide and 50 ml of water were added (the solution was 10% with respect to the NaOH content).

b) 0.1 g of the substance was dissolved in 70 ml of alcohol, the amounts of the remaining reagents were added as calculated from a hydrolysis with 20% alkali. The duration of the experiment was about 1.5 hours. The results of the experiments in an alcohol medium were analogous to those obtained in the first experiment without alcohol.

3. Experiment on the Hydrolytic Cleavage of the Amino-group in 2-Methoxy-6-chlor-9-aminoacridine by Hydrochloric Acid.

0.1 g of 2-methoxy-6-chlor-9-aminoacridine was dissolved in a mixture of 40 ml of concentrated hydrochloric acid and 100 ml of water. The mixture was boiled for 1 hour with a reflux condenser. After cooling, the flask was fitted with a still head and dropping funnel for the addition of the solution of alkali; the reflux condenser was placed in an inclined position, to the liquid in the flask 60 ml of a concentrated solution of sodium hydroxide and 100 ml of water were added by means of the dropping funnel and then upon boiling, the water distilled into the receiver containing water and indicator. The amount of titrated HCl used for the neutralization of the ammonia evolved was equal to the amount of acid used in the hydrolysis in water and in alcoholic alkali. Three experiments gave 1.5, 1.6 and 1.7 ml of N/10 HCl used for the neutralization of the ammonia evolved. These model experiments showed that even considerable variations in the experimental conditions did not alter the magnitude of the figures obtained for the amount of ammonia evolved.

1-Chlor-9-aminoacridine

Experiment 1.

0.1005 g substance: heated with 60 ml of 48% alkali and 250 ml water. Length of boiling 1 hour 20 minutes.

For 100 ml of distillate were used up 3.9 ml N/10 HCl.
" 150 " " " " " " 5.5 " N/10 HCl
" 200 " " " " " " 6.3 " N/10 HCl

Experiment 2.

0.1 g substance: heated under the same conditions for 1 hour 20 minutes.

For 100 ml of distillate were used up 4.2 ml N/10 HCl.
" 150 " " " " " " 5.8 " N/10 HCl.
" 200 " " " " " " 6.4 " N/10 HCl.

2-Chlor-9-aminoacridine

Experiment 1.

0.1015 g substance: heated under the same conditions.

For 100 ml of distillate were used up 3.4 ml N/10 HCl.
" 150 " " " " " " 4.8 ml N/10 HCl.
" 200 " " " " " " 5.4 ml N/10 HCl.

Experiment 2.

0.1008 g substance: heated under the same conditions.

For 100 ml of distillate were used up 3.4 ml N/10 HCl.
" 150 " " " " " " 4.9 " N/10 HCl.
" 200 " " " " " " 5.6 " N/10 HCl.

Experiments with 3-chlor-9-aminoacridine, 4-chlor-9-aminoacridine and 9-aminoacridine were

performed under these conditions. All the data obtained are given in Table 2, the last column showing the final results.

## CONCLUSIONS

1. The relative rate of hydrolysis was investigated of aminogroups in four chlor-isomers of 9-aminoacridines and their analog not containing chlorine which are "stem substances" of the chlor-isomers of 9-(dialkylaminoalkyl)-aminoacridines, exhibiting different activities towards Plasmodium relictum, and of aminogroups in the methyl derivative of the 3-chlor-isomer.

2. In connection with the rearrangement of the isomeric chloraminoacridines into the quinoid form, the figures on the rate of hydrolysis do not indicate the possibility of finding a relationship between their rate of hydrolysis ("degree of quinoidness") and the antiplasmodial activity of those compounds the stem substances of which are the investigated isomers of chlor-9-aminoacridine. The figures obtained disclaim the "quinoid hypothesis" of antiplasmodial activity, propounded by Schonhofer.

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# DERIVATIVES OF ZINGERONE - II

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In a study of the influence of chemical structure on the intensity of the burning taste of substances similar to zingerone, we showed ** that the presence of phenol hydroxyl in the molecule was unconditionally necessary for the appearance of the burning properties of this type of compound.

In this connection we considered it of interest to synthesize a series of compounds of analogous structure containing hydroxyl groups of different reactivities, and to compare the intensity of their effect on the taste.

Quantitative data, characterizing the degree of burning of the compounds we obtained were determined by means of tasters,** and are shown in the table.

As is evident from the table, the changes we produced in the molecular structure of zingarone, principally in its aromatic portion, result in all cases in a weakening of the intensity of the burning taste. The introduction of a second hydroxyl group in place of the methoxyl (I), and also the introduction in the aromatic nucleus of a nitrogroup in an ortho-position to the hydroxyl (III, IV) result in a considerable decrease and a complete destruction of the activity. From this it may be concluded that an increase in the acidic nature of the molecule results, in the given case, in a drop in the burning effect. This result is also obtained where a second hydroxyl group is introduced into the ω-position of the side chain (II).

A comparative study of the intensity of the burning taste further indicates that zingarone (X), in which the methoxyl group is found in an ortho-position to the hydroxyl, possesses a greater activity than either p-hydroxyphenylethylmethylketone (VI), not containing a methoxyl group, or isozingerone (V), in which the hydroxyl group is found in a meta-position to the chain. Thus it may be concluded that a para-position of the hydroxyl group in relation to the side chain as well as the presence of a methoxyl group in the nucleus favor an intensification of the burning taste. Murai [1] also indicates a weakly-burning taste for m-hydroxyphenylethylmethylketone, but his report on the extremely strong taste effect of isozingerone differs from our data. Also incorrect is the statement by Nomura and Nosawa [2] that the presence of a hydroxyl has in general no influence on the sharp taste in this group of compounds.

It shouldbe noted that in the case of p-hydroxyphenylethylmethylketone, the qualitative nature of the variation in the degree of burning with a corresponding change in molecular structure remains the same as for zingerone. Alkylization of the phenyl hydroxy group results in a destruction of the activity (VII), and a lengthening of the side chain connected to the carbonyl group results in an intensification of the sharp taste (VIII).

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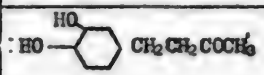
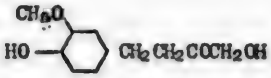
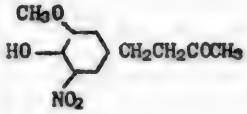
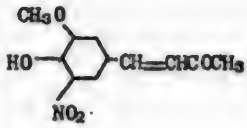
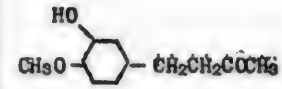
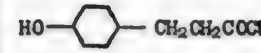
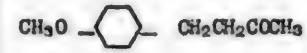
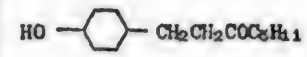
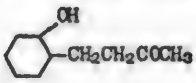
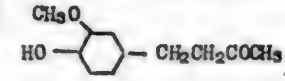
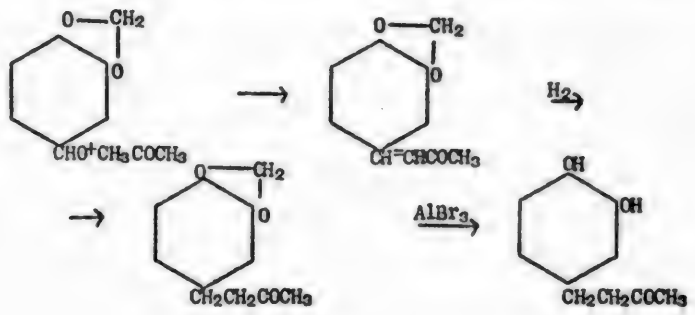
* Deceased.

** See previous paper, J. Gen. Chem. USSR, 18, 1386 (1948).

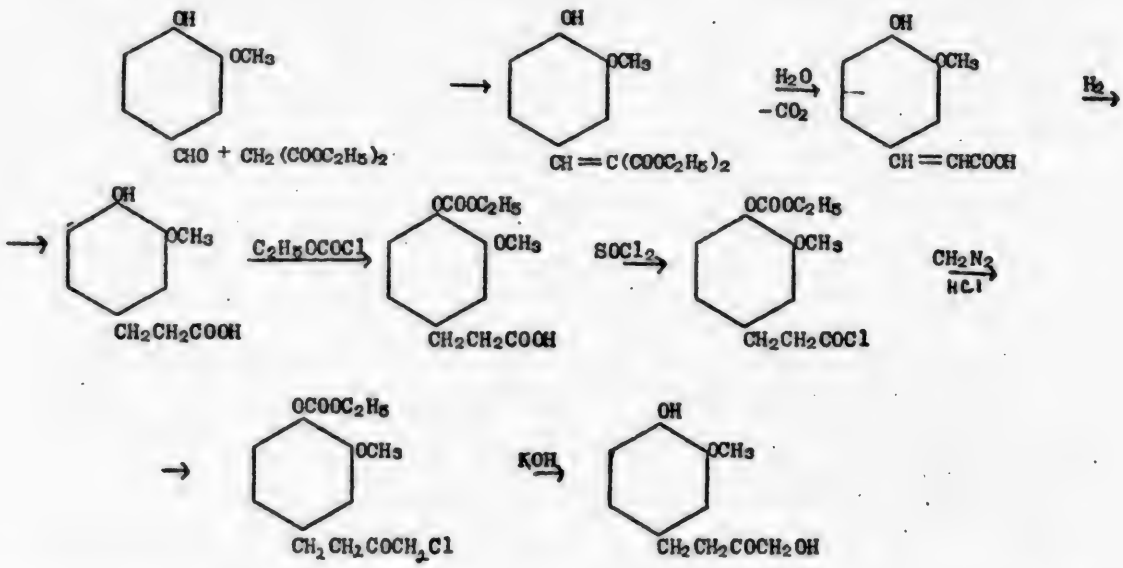
| Exp. No. | Name of Compound | Formula | Degree of burning |
|---|---|---|---|
| I | 3,4-dihydroxyphenylethylmethylketone |  | 2 |
| II | 4-hydroxy-3-methoxyphenylethyloxy-methylketone (ω-hydroxyzingerone) |  | < 1 |
| III | 4-Hydroxy-3-methoxy-5-nitrophenyl-ethylmethylketone (5-nitro-zingerone) |  | < 1 |
| IV | 4-Hydroxy-3-methoxy-5-nitrostyryl-... methylketone |  | < 1 |
| V | Isozingerone (4-methoxy-3-hydroxy-phenylethylmethylketone) |  | 3 |
| VI | p-Hydroxyphenylethylmethylketone |  | 2,5 |
| VII | p-Methoxyphenylethylmethylketone |  | < 1 |
| VIII | p-Hydroxyphenylethylisoamylketone |  | 5.5 |
| IX | o-Hydroxyphenylethylmethylketone |  | 3 |
| X | Zingerone |  | 9 |

The synthesis of 3,4-dihydroxyphenylethylmethylketone was accomplished by means of piperonyl-acetone:



since all attempts to obtain it by the usual method from protocatechualdehyde and aldehyde were unsuccessful, which agrees with the findings of Buck and Heilbron [3]; Pearson's [4] report on the preparation of 3,4-dihydroxystyrylmethylketone from protocatechualdehyde and acetone in sodium hydroxide solution is completely at variance with our data.

For the preparation of ω-hydroxyzingerone (II) we started with the chloranhydride of carbethoxyhydroferulic acid, synthesized according to the data in the literature [5, 6], and diazomethane. As a result of a hydrolysis of the carbethoxy-ω-chlorzingerone so obtained there occurred a simultaneous cleavage of the carbethoxyl group and of a haloid atom with the formation of the dihydroxyderivative. Thus, the complete synthesis of this compound was accomplished according to the following scheme:




4-Hydroxy-3-methoxy-5-nitrophenylethylmethylketone (5-nitrozingerone) (III) was obtained by the action of nitrogen oxides upon an ether solution of zingerone.

The remaining substances, that is: 4-hydroxy-3-methoxy-5-nitrostyrylmethylketone (IV), 3-hydroxy-4-methoxyphenylethylmethylketone (isozingerone) (V), 4-hydroxyphenylethylmethylketone (VI), 4-hydroxy-phenyl-ethylisoamylketone (VIII) and 2-hydroxyphenylethylmethylketone (IX), were synthesized by the usual scheme:

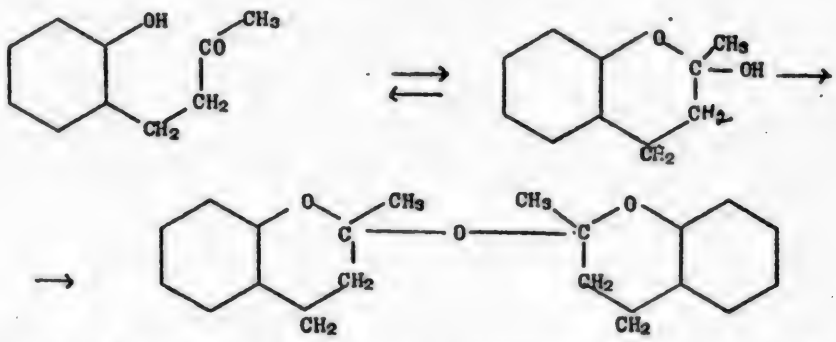
$$R-CHO + CH_3COR' \longrightarrow R-CH=CHCOR' \xrightarrow{H_2} R-CH_2-CH_2-CO-R',$$

by the condensation of the corresponding hydroxyaldehyde with methyl ketone in an alkaline medium and a subsequent reduction of the styryl ketone thus formed (with the exception of compound IV [6]).

It is of interest to note that in one of the first experiments on the preparation of o-hydroxyphenylethylmethylketone, upon purification of the final product obtained by vacuum distillation, at 15 mm. pressure the o-hydroxyphenylethylmethylketone experienced a considerable change. The separation of drops of water was observed and the distillate was colored violet. The observations of Nomura and Nosawa [2] on the boiling point of o-hydroxyphenylethylmethylketone at 14.5 mm. do not agree with our observations of the change taking place upon vacuum distillation of this substance.

From the distillate which crystallized upon standing we were able to separate a crystalline

colorless substance. By its properties, results of analysis and determination of molecular weight, this substance was shown to be the ether of 2-hydroxy-2-methylchroman*, appearing as the tautomer of o-hydroxyphenylethylmethylketone.



It was therefore necessary to purify the o-hydroxyphenylethylmethylketone by another method, that is by recrystallization from petroleum ether.

The o-methoxyphenylethylmethylketone obtained from o-hydroxyphenylethylmethylketone was also distinguished by its instability in comparison with p-methoxyphenylethylmethylketone, and darkened upon standing, as a result of which the results obtained for the methoxyl group content in this compound are shown to be at variance with the calculated data.

## EXPERIMENTAL

### 3,4-Dihydroxyphenylethylmethylketone (I)

A solution of 8 g of piperonylacetone in 25 ml of dry nitrobenzene was mixed with a solution of 23 g of aluminum bromide in 25 ml of nitrobenzene. The next day the reaction mixture was poured into 400 ml of water, and slightly acidified with hydrochloric acid. The mixture was extracted with ether and the ether solution shaken with 200 ml of 10% solution of sodium hydroxide. The alkaline solution was washed with ether to remove the nitrobenzene and neutralized to Congo with hydrochloric acid. The product was extracted several times with ether, the ether solution dried with anhydrous sodium sulfate and the solvent distilled. The residue was redistilled in a vacuum in a current of nitrogen. B.p. 220-221° at 8 mm. A thick oil was obtained which crystallized upon standing. The product was purified by solution in absolute ether and precipitation with petroleum ether. Colorless, prismatic crystals, m.p. 85.5 -86°. Yield of the pure substance was 1.5 g.

0.1473 g substance: 0.3610 g $CO_2$: 0.0888 g $H_2O$.
Found %: C 66.84; H 6.75.
$C_{10}H_{12}O_3$. Calculated %: C 66.67; H 6.67.

### ω-Hydroxyzingerone (4-hydroxy-3-methoxyphenylethyl-oxymethylketone) (II)

a) 4-Carbethoxy-ω-chlorzingerone. Hydroferulic acid was obtained from vanillin and malonic ester [5] and purified by redistillation in vacuo. B.p. 215° at 13 mm.; m.p. 89°. Carbethoxy-hydroferulic acid was obtained by the action of ethylcarbochlor ester in the presence of alkali [6], with a yield of 97%. M.p. 88°. The chloranhydride of this acid was obtained by the action of thionyl chloride. After distilling the excess thionyl chloride in vacuo, a dark-yellow oily liquid remained, which could not be further purified. The yield was 85.9% of theoretical, based on hydroferulic acid.

To a solution of 18 g of unpurified chloranhydride of carbethoxyhydroferulic acid in 250 ml of absolute ether were added an ether solution of diazomethane, obtained from 27 ml of N-nitrosomethyl-

* Somewhat later Baker and Walker [7] observed the formation of the methyl and ethyl ethers of hydroxy-methylchroman upon reduction of o-hydroxybenzylidene acetone in methyl or ethyl alcohol.

urethan in 270 ml of absolute ether and 55 ml of a 25% solution of potassium hydroxide in methyl alcohol. The next day the ether was removed in the cold in vacuo, after which a dry yellowish crystalline substance remained, evidently the diazoketone. The product was dissolved in the cold in 180 ml of glacial acetic acid, after which 20 ml of concentrated hydrochloric acid was added dropwise to the cooled solution, at which a profuse evolution of gas was observed. The solution thus obtained was poured with mixing into 2 liters of water. A crystalline precipitate formed which was separated and recrystallized three times from benzene (b.p. 50-85°). Lightly cream-colored crystalline powder, m.p. 92-93°. Yield 12 g, i.e. 63.5% of the theoretical figuring on the chloranhydride of carbethoxyhydroferulic acid.

4.105 mg substance: 8.520 mg $CO_2$; 2.100 mg $H_2O$.
3.120 mg substance: 6.457 mg $CO_2$; 1.632 mg $H_2O$.
4.217 mg substance: 2.020 mg AgCl.
Found %: C 56.60, 56.45; H 5.72, 5.85; Cl 11.85.
$C_{14}H_{17}O_5Cl$. Calculated %: C 55.91; H 5.66; Cl 11.81.

b) ω-Hydroxyzingerone (4-hydroxy-3-methoxyphenyl ethyloxymethylketone). To 9 g of 4-carbethoxy-3-methoxyphenylethylchlormethylketone was added 120 ml of a 1 N. solution of sodium hydroxide, after which the mixture was heated over an open flame to dissolve the precipitate. After filtering and acidifying the alkaline solution the product was extracted with ether and the ether solution dried with anhydrous sodium sulfate. After distillation of the ether the residue was redistilled under high vacuum, at which a fraction was collected boiling at 180-185° at 1 mm or 173-178° at 0.6 mm. The yield was 3 grams. The substance crystallized in the receiver. After a double recrystallization from chloroform colorless crystals were obtained, m.p. 113.5-114°.

2.830 mg substance: 6.512 mg $CO_2$; 1.639 mg $H_2O$.
10.82 mg substance: 2.14 ml $CH_4$ (0°, 760 mm).
Found %: C 62.76; H 6.48; H' 0.88.
$C_{11}H_{14}O_4$: Calculated %: C 62.9; H 6.7; H 0.95.

5-Nitrozingerone (III) (4-hydroxy-3-methoxy-5-nitrophenylethylmethylketone)

Into a solution of 3 g of zingerone in 60-70 ml of water was passed a stream of nitric oxide formed by the action of 40% sulfuric acid on sodium nitrite. A slight precipitate was filtered off, and the solvent removed from the filtrate under vacuum in the cold. The residue was pressed on a porous plate and for purification, several times recrystallized from a mixture of benzene and cyclohexane. Orange, needle-shaped crystals, m.p. 101.5-102°.

4.954 mg substance: 0.255 ml $N_2$ (25.5°, 755 mm).
Found %: N 5.71.
$C_{11}H_{13}O_5N$. Calculated %: N 5.85.

4-Hydroxy-3-methoxy-5-nitrostyrylmethylketone (IV)

A solution of 10 g of 5-nitrovanillin (m.p. 175°; obtained by passing nitric oxide into an ether solution of vanillin) in 90 ml of acetone was mixed with 25 ml of a 10% solution of sodium hydroxide and to the crystalline paste formed was added water to the complete solution of the precipitate. After 8 days the dark-colored solution was filtered and acidified to Congo with hydrochloric acid. The precipitate which formed was separated, washed with water and dried at 100°. Yield, 10.5 g. After a double recrystallization from acetone the product appeared as orange, needle-shaped crystals, m.p. 159°.

4.138 mg substance: 0.235 ml $N_2$ (25.5°, 753 mm).
3.732 mg substance: 0.205 ml $N_2$ (21°, 754 mm).
Found %: N 6.29; 6.25.
$C_{11}H_{11}O_5N$. Calculated %: N 5.91.

Isozingerone (4-methoxy-3-hydroxyphenylethylmethylketone) (V) [1, 9]

To a solution of 2.4 g of isovanillin in 10 ml of acetone was added 7 ml of a 10% solution of sodium hydroxide, after which the mixture was allowed to stand for 4 days at room temperature. 10 ml of water were then added and the styryl ketone precipitated with a small excess of hydrochloric acid. The impure 4-methoxy-3-hydroxystyrylmethylketone was reduced in 60 ml of water with 25 g of a 3% sodium amalgam, and the reaction product separated as usual. B.p. 165-167° at 7 mm.

The isozingerone crystallized upon cooling and was recrystallized from a mixture of absolute ether and petroleum ether. Colorless, prismatic crystals, m.p. 41-42.5°. Yield, 0.7 g.

p-Hydroxyphenylethylmethylketone (VI). [2]

To a solution of 34 g of p-hydroxybenzaldehyde in 230 ml of 10% sodium hydroxide was added 35 g of acetone and the mixture allowed to stand at room temperature for 4 days. Upon acidifying the solution a precipitate of p-hydroxystyrylmethylketone was formed which was separated, washed with water and dried. The impure styryl ketone was reduced in 1 l. of water with 483 g of 3% sodium amalgam with vigorous stirring. Upon completion of reduction and removal of mercury the solution was acidified and the reaction product which separated was extracted with ether. The ether solution was dried with anhydrous sodium sulfite, the ether distilled off and the residue distilled in vacuo, upon which a fraction was collected boiling at 190-210° at 18 mm. The crystallized product was recrystallized from ligroin, m.p. 82-83°. Yield, 9 g.

p-Methoxyphenylethylmethylketone (VII) [2]

A solution of 2 g of p-hydroxyphenylethylmethylketone in 7 ml of 10% sodium hydroxide was shaken with 1.5 g of dimethyl sulfite for one-half hour. The product was extracted with ether, dried and distilled. B.p. 163-167° at 19 mm. Yield, 1.5 g.

p-Hydroxyphenylethylisoamylketone (VIII)

A mixture of 20 g of p-hydroxybenzaldehyde, 20 g of methylisoamylketone and a solution of 14 g of sodium hydroxide in 500 ml of water was shaken at room temperature for 70 hours. The liquid was washed with ether, from which 10 g of methylisoamylketone was recovered. The aqueous solution was acidified, extracted with ether, the ether solution shaken with a 15% solution of bisulfite, then washed with water and dried with anhydrous sodium sulfite. After removal of the ether the basic mass of p-hydroxystyrylisoamylketone was distilled at 220-223° and 1.6 mm. The crystallized distillate was recrystallized from benzene. M.p. 81-82°. Yield 7 g.

0.1053 g substance: 0.3010 g $CO_2$; 0.0763 g $H_2O$.
0.1037 g substance: 0.2954 g $CO_2$; 0.0760 g $H_2O$.
Found %: C 77.95, 77.69; H 8.11, 8.20.
$C_{14}H_{18}O_2$: Calculated %: C 77.06; H 8.25.

6 g of the styrylketone was reduced in 125 ml of water with 100 g of 3% sodium amalgam. After the usual treatment, i.e. acidification with hydrochloric acid and extraction with ether, there was separated out a small quantity (about 1 g.) of a yellow oil, b.p. 185-190° at 1.1 mm., not crystallizing either upon long standing or upon cooling.

p-Nitrophenylhydrazone - thin, yellow needles, crystallizing from dilute alcohol, m.p. 133.5-134°.

4.578 mg. substance. 0.452 ml $N_2$ (18°, 744 mm).
3.803 mg substance: 0.382 ml $N_2$ (21°, 743 mm).
Found %: N 11.34; 11.41.
$C_{20}H_{25}O_3N_5$. Calculated %: N 11.83.

o-Hydroxyphenylethylmethylketone (IX) [2,9,10]

A mixture of 50 g of salicylaldehyde, 340 ml of a 10% solution of sodium hydroxide and 50 g of acetone were diluted with water to 2 l. and allowed to stand at room temperature for 3 days. Upon acidification with hydrochloric acid, a yellow, granular precipitate was formed. The product was steam distilled, upon which the small quantity of unreacted salicylaldehyde was distilled off. The residue was removed, dried (40.6 g) and recrystallized with animal charcoal from benzene. M.p. 139-140°.

40 g of the o-hydroxyphenylethylmethylketone so obtained was reduced in 800 ml of water with 340 g of 3% sodium amalgam, as usual. The product which separated upon acidification was extracted with ether. The residue crystallized upon removing the ether and was recrystallized from petroleum ether. M.p. 46-47°. Yield, 15 g.

### 2-Hydroxy-2-methylchromyl ether

Upon distilling o-hydroxyphenylethylmethylketone in vacuo at 15 mm. pressure a change in the substance being distilled took place with separation of drops of water. From 85 to 100° the distillate was colorless, from 100 to 150° it changed to a rose color, and over 150° the product began to decompose. Upon cooling, the distilled substance crystallized and was recrystallized from alcohol. Colorless, lamellated crystals, m.p. 95°. The substance was insoluble in a 10% solution of sodium hydroxide.

0.1480 g substance: 0.4194 g $CO_2$; 0.0930 g $H_2O$.
0.1473 g substance: 0.4176 g $CO_2$; 0.0906 g $H_2O$.
Found %: C 77.29, 77.32; H 7.03, 6.88.
$(C_{10}H_{11}O)_2O$. Calculated %: C 77.42; H 7.10.

0.4824 g substance: 18.82 g benzene; $\Delta t$ 0.4325°.
0.3764 g substance: 21.63 g benzene; $\Delta t$ 0.3011°.
Found: M 312.5, 304.7.
$(C_{10}H_{11}O)_2O$. Calculated: M 310.

### o-Methoxyphenylethylmethylketone

A solution of 13 g of o-hydroxyphenylethylmethylketone in 40 ml of 10% sodium hydroxide was shaken for 45 minutes with 10 g of dimethyl sulfate. The product was extracted with ether, the ether extract dried with anhydrous sodium sulfate, and the solvent distilled off. The residue was distilled in vacuo. B.p. 137-139° at 14 mm; 140-142° at 15 mm; 149-150° at 21 mm. It darkened upon standing in air.

30.8 mg substance: 9.0 ml. N/10 $Na_2S_2O_3$.
20.8 mg substance: 6.2 ml N/10 $Na_2S_2O_3$.
Found %: ($OCH_3$) 15.08, 15.38.
$C_{10}H_{11}O(OCH_3)$. Calculated %: ($OCH_3$) 17.41.

The unsatisfactory results are evidently related to the instability of the substance.

## CONCLUSIONS

1. A series of compounds was synthesized differing from zingerone chiefly by the nature and position of the substituents in the aromatic nucleus.

2. It was established that an increase in the acidic nature of the phenyl hydroxyl group, an accumulation of hydroxyl groups in the molecule and also a change in the position of the substituents in the aromatic nucleus of zingerone were shown, in the cases investigated, to have a negative influence on the intensity of the burning taste.

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